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## ABSTRACT

The Effect of Humidity on the Collection Efficiency for  
Oxygenated Compounds Adsorbed on Activated Charcoal.

(August 1990)

Robert Bruce Walton, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Richard B. Konzen

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Charcoal tubes were exposed to four solvents individually at two levels of humidity and two solvent concentrations. The tubes were first exposed to a zero contaminant concentration at a set humidity level of 50 or 80 % for two hours. Immediately following, they were exposed to the same humidity level along with a predetermined solvent concentration, either 50 or 200 ppm, for an additional two hours.

With the exception of ethyl ether, all humidity and concentration combinations caused a decrease in the

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collection efficiency. Statistically significant differences were shown to exist between compound types, humidity, and concentration levels. As the humidity level increased the collection efficiency decreased and decreasing contaminant concentration caused a decrease in collection efficiency. The compound effect was clearly shown to be related to water solubility as the most hydrophilic compounds were more highly affected by humidity.



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**THE EFFECT OF HUMIDITY ON THE COLLECTION EFFICIENCY FOR  
OXYGENATED COMPOUNDS ADSORBED ON ACTIVATED CHARCOAL**

**A Thesis**

**by**

**ROBERT BRUCE WALTON**

**Submitted to the Office of Graduate Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE**

**August 1990**

**Major Subject: Industrial Hygiene**



**THE EFFECT OF HUMIDITY ON THE COLLECTION EFFICIENCY FOR  
OXYGENATED COMPOUNDS ADSORBED ON ACTIVATED CHARCOAL**


A Thesis

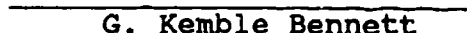
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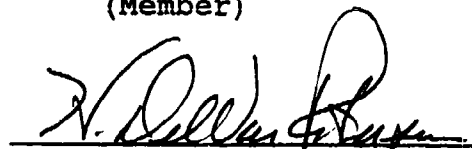
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August 1990

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**TABLE OF CONTENTS**

	Page
<b>ABSTRACT.....</b>	<b>iii</b>
<b>ACKNOWLEDGMENT.....</b>	<b>v</b>
<b>TABLE OF CONTENTS.....</b>	<b>vi</b>
<b>LIST OF TABLES.....</b>	<b>viii</b>
<b>INTRODUCTION.....</b>	<b>1</b>
<b>LITERATURE REVIEW.....</b>	<b>4</b>
Activated Carbon.....	4
Adsorption Theory.....	9
Adsorption on Activated Charcoal.....	17
Charcoal Tubes.....	20
Relative Humidity Effects.....	21
Concentration Effects.....	29
Polarity Effects.....	30
The Problem.....	32
<b>METHODOLOGY.....</b>	<b>33</b>
Overview.....	33
Contaminants.....	33
Sampling Devices.....	34
Contaminant and Water Vapor Generation.....	34
Sampling Bag.....	36
Experimental Procedure.....	37
Analysis.....	40
<b>RESULTS AND DISCUSSION.....</b>	<b>42</b>
<b>CONCLUSIONS AND RECOMMENDATIONS.....</b>	<b>54</b>

**TABLE OF CONTENTS (Con't)**

	<b>Page</b>
<b>REFERENCES.....</b>	<b>56</b>
<b>APPENDIX A.....</b>	<b>59</b>
<b>APPENDIX B.....</b>	<b>61</b>
<b>APPENDIX C.....</b>	<b>63</b>
<b>APPENDIX D.....</b>	<b>68</b>
<b>APPENDIX E.....</b>	<b>71</b>
<b>APPENDIX F.....</b>	<b>77</b>
<b>APPENDIX G.....</b>	<b>86</b>
<b>APPENDIX H.....</b>	<b>88</b>
<b>VITA.....</b>	<b>105</b>

## LIST OF TABLES

	Page
Table I     Sampling Parameters for a Run.....	39
Table II    Collection Efficiencies for Ethyl Ether....	43
Table III   Collection Efficiencies for Ethyl Acetate..	44
Table IV    Collection Efficiencies for..... 2-Methoxyethanol	45
Table V     Collection Efficiencies for Propanol.....	46
Table VI    Mean Collection Efficiencies..... (Ether and Acetate)	49
Table VII   Mean Collection Efficiencies..... (2-Methoxy and Propanol)	50

## INTRODUCTION

Industrial hygiene is a science based on the anticipation, recognition, evaluation, and control of occupational exposures to chemical, physical, and biological agents in the industrial environment. A trained industrial hygienist must be familiar with the particular industrial operation and anticipate what type of hazards may be present in that workplace. Furthermore, during the industrial hygiene survey, he must recognize all hazards which exist both anticipated and unexpected, determine which hazards require further evaluation, and recommend control methods for eliminating or reducing the hazard. In many cases, the evaluation step involves determining an estimated concentration of chemical agents to which personnel are exposed. The most common and accurate method available to the industrial hygienist for determining gaseous chemical agent exposure levels is contaminant capture via solid adsorbents.

Of the solid adsorbents commercially available, charcoal tubes, containing activated charcoal, appear to be the most widely used collection method for monitoring organic vapors in the workplace. This sampling method is based on drawing a known volume of air at a constant flow

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rate through the charcoal tube where the organic contaminants are adsorbed onto the charcoal. A battery-powered pump is used to generate the required air flow and the charcoal tube is located in the worker's breathing zone. After collection, the contaminants are solvent desorbed and analyzed by gas chromatography. The National Institute for Occupational Safety and Health (NIOSH) has adopted this technique for more than one hundred individual chemicals.<sup>(1)</sup>

One problem with using any adsorbent as a collection media is its ability to adsorb additional undesired vapors. An excellent example is the collection of organic vapors in a humid environment. The activated charcoal readily adsorbs the organic vapors; however, research has shown the water vapor present will act as an interferent in the adsorption process with the degree of interference dependent on contaminant concentration present. The degree of interference increases with increasing relative humidity.<sup>(2)</sup>

The undertaking of this research project was initiated as a result of a previous thesis by Lori A. Rushlow. She showed that the collection efficiency of organic vapors on charcoal tubes decreased with increasing relative humidity. Furthermore, this observed decrease was exaggerated for the oxygenated compound, acetone, as compared to the non-oxygenated compound, toluene.<sup>(3)</sup>

The purpose of this research was to investigate the effect an initial exposure of relative humidity had on the collection efficiency of charcoal tubes for four oxygenated

compounds.

## LITERATURE REVIEW

### Activated Carbon

The adsorptive capabilities of carbon have been recognized and documented for a long time. The Egyptian's, in 1550 B. C., used various carbons for medicinal purposes and Kehls, in 1793, used charcoal to remove bad odors from gangrenous ulcers. The most common adsorptive carbon sources were blood char, coconut char, bone char, and lignite char. In 1822, Bussy increased the adsorptive power of blood char twenty to fifty times through a heating process which ultimately led to the development of activated carbon. (4)

A patented invention by Ostrejko in 1900 began the development of modern commercial activated carbon. However, the first activated carbon produced in America was developed accidentally from an endeavor to find utility for leached black-ash. (4) At this time, the only industrial application for activated carbon was for use in the sugar cane industry. It was believed that powdered carbon could be applied to raw sugar cane juice to eliminate an intermediate step in the production of crystallized sugar. Unfortunately, this manufacturing method never materialized and work with activated carbon nearly ceased.

Hunter, in 1865, and others demonstrated the ability of charcoal to adsorb gases. However, it was not until an

event during World War I, in 1915, that this capability was truly recognized. The Germans initiated chemical warfare and activated charcoal was used in air purifying respirator canisters to protect troops against toxic gases. The publicity surrounding this new finding stimulated much research into new fields of use for activated carbon.(4,5,6)

Activated carbon is essentially a special form of amorphous carbon deposited at low temperatures and free from adsorbed hydrocarbons which are normally associated with it and reduces its power to adsorb other substances. Although numerous patents have been granted for preparing activated carbon, they all describe a different way of conducting a basic procedure. A carbon source material is carbonized under controlled conditions and subjected to the action of an oxidizing gas, such as steam or air at elevated temperatures. Its final properties are influenced by the source material used and by the conditions of activation. Therefore, the term activated carbon does not define a single chemical entity but is instead a generic name for a class of substances.(4,6)

During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by pyrolytic decomposition of the starting material, and the freed atoms of elementary carbon are grouped into organized crystallographic formations. However, the grouped arrangement of crystals is irregular and the free interstices between them become filled with tar. The

resulting product has only a very small adsorption capacity.<sup>(7)</sup> There are many ways to increase the adsorptive capabilities of the carbon and they are grouped into two main categories; chemical and physical activation.

The carbon source used during chemical activation consists predominantly of cellulose and the advantage is that a good activated carbon can be produced in a single operation. A chemical activation agent which influences the pyrolytic process is added to the initial carbonaceous material prior to carbonization. The temperature required for pyrolysis is lowered, the amount of tar formed and aqueous phase in the distillate are reduced, and the yield of carbon in the final product is increased. The most commonly used activation agents are zinc chloride, potassium sulphide, potassium thiocyanate, phosphoric and sulphuric acid. In fact, the most widely used activated carbon for industrial hygiene purposes is based on coconut shell chemically activated by zinc chloride.<sup>(7)</sup>

The action of the activating agent causes the cellulose to swell during which lateral bonds are broken resulting in an increase in the inter- and intra-micelle voids. The degree of impregnation, the weight ratio of the anhydrous activation salt to the dry starting material, is the critical factor in determining the porosity of the final product because the volume of salt in the carbonized material equals the volume of pores freed by its extraction. Chemical activation is generally carried out at temperatures

between 400 and 1000 degrees Celsius. The optimum temperature for zinc chloride is 600 degrees Celsius which is moderately lower than that required for physical activation and therefore greatly promotes the development of the microporous structure. (7)

Physical activation is a two step process with the first step being carbonization which is critical to the activation and quality of the final product. The initial phase of carbonization requires a temperature of 170° C at which the material is being dried without degradation. The next phase requires a temperature of 275° C where exothermal decomposition begins and a considerable amount of tar is generated. The final phase requires heating at 400-600° C after which the product carbon content reaches 80%. (4,6,7)

The second step is activation of the carbonized material through an activation agent, most often steam, carbon dioxide, or oxygen. This leads to the removal of unorganized carbon, the non-uniform burn-out of elementary crystals, and the formation of new pores. As activation continues, complete burn-out of the walls between adjacent micropores occurs which leads to an increase in transitional and macropores. According to Dubinin, when the burn-off is less than 50% a microporous, active carbon is obtained, when it is greater than 75% a macroporous product is obtained, and when the burn-off is in between, the product is of mixed structure and contains both micro- and macropores. (7)

Activation with steam is carried out at temperatures from 750 to 950° C with the exclusion of oxygen, which at these temperatures aggressively attacks carbon and decreases the yield by surface burn-off. Activation with carbon dioxide involves a less energetic reaction than that with steam and requires a higher temperature (850-1100° C). In actual practice, the agent used is flue gas with a small amount of steam added and is a case of combined activation. The use of oxygen as an activation agent is beset with a number of difficulties and is rarely used. However, carbon activated with oxygen has a large amount of surface oxides which have been found to be active sites for adsorption of polar compounds. (4,7)

Currently, there are many varied uses for activated carbon both in the granular and powdered forms. Granular activated carbon has gained wide acceptance for air purification, both in respirator cartridges and air recirculation systems, solvent recovery, and water purification and odor removal. Powdered activated carbon is used in water purification, liquid decolorization, and as a treatment alternative in certain cases of internal human poisoning. The newest technological developments have been the use of granular activated carbon for safe application of systemic insecticides and as a method to concentrate medicinal drugs.

### Adsorption Theory

The discovery of the adsorption process as now understood, is generally attributed to Scheele who in 1773 was the first to describe experiments on gases exposed to carbon.<sup>(4)</sup> Since then, many experiments and much research has been conducted to study the phenomenon of adsorption.

Adsorption is a physical or chemical process where a substance accumulates at an interface between phases. The phase interface may be either solid-vapor or solid-liquid and its composition is different from that of either bulk phase. The accumulating substance, termed the adsorbate, has a tendency to collect on the surface of the solid, termed the adsorbent.<sup>(6,7,8)</sup> If adsorption occurs at constant volume, the pressure drops; if at constant pressure, the volume decreases.<sup>(9)</sup>

Once a substance collects at the surface of a solid, two things can happen. The substance either remains adsorbed on the surface of the solid (this surface includes the external, geometrical surface, and the internal surface formed by the walls of the pores) or it can penetrate into the structure of the solid, sometimes even between the atoms of its crystal lattice, producing a solid-solution termed absorption. Adsorption can be further differentiated from absorption in that adsorption usually occurs without a chemical reaction between the adsorbent and the adsorbate, while absorption involves a permanent chemical reaction or



phase change. Many times it is difficult to determine the final resting place of the molecules and therefore a general term "sorption" has been coined to apply when a gas, vapor, or liquid is taken up by a solid. (6,7,9)

Adsorbed molecules are held at the surface by one of two different forces. There is either a weak interaction between the adsorbent and adsorbate, similar to condensation, or a strong interaction, similar to chemical reactions. The weak interaction is called physical adsorption and the strong interaction is chemical adsorption. (6,7,9)

Physical, or van der Waals adsorption is caused by forces similar to those that cause condensation of vapors to a liquid and is determined by three factors: the heat of adsorption, the surface of the adsorbent, and the pore structure of the adsorbent. The chemical nature of the adsorbed molecules remain unchanged and the forces are identical to the intermolecular forces of cohesion which operate in the solid, liquid, and gaseous state. These forces are electrostatic in nature, and we now know that there are three effects that jointly account for the attractive forces: the orientation effect of Keesom, the induction effect of Debye, and the dispersion effect of London. The orientation effect is based on the fact that many uncharged molecules have dipole moments, which when properly oriented, will lead to the development of attractive forces. It is of significance only in the mutual

interaction of highly polar molecules possessing permanent dipoles and is inversely proportional to the temperature. The induction effect is caused by a permanent dipole inducing polarization of molecules situated in its proximity; it is independent of the temperature. These two effects explain how van der Waals attractive forces are developed in highly polar compounds but they do not help explain attractive forces found in molecules which possess no permanent dipoles. The London dispersion effect explains those attractive forces. Molecules without a permanent dipole have fluctuating dipoles which gives rise to a fluctuating electric field. When two molecules with fluctuating dipoles come close to one another their total energy decreases, and this is the reason for their mutual attraction. The attractive force decreases with the seventh power of the distance and is independent of the temperature. In most cases of physical adsorption, the dispersion effect is the governing van der Waals attractive force. (4,6,7,9)

Physical adsorption occurs with a much lower evolution of heat during the adsorbate/adsorbent interaction, generally of the same order of magnitude as for heat of condensation, than for chemisorption. In addition, it does not proceed at temperatures much higher than the boiling point of the adsorbate, does not require any activation energy, is non-specific, and is capable of multimolecular adsorption. (4,6,7,9) These characteristics are of great importance since they allow the adsorbate to be desorbed

from the adsorbent unaltered.

Chemical adsorption or chemisorption, also termed activated adsorption because it requires an activation energy much like that seen in chemical reactions, results from the exchange or sharing of electrons between the adsorbate and the surface of the adsorbent. The bond formed between the adsorbate and adsorbent is essentially a chemical bond and is therefore much stronger than in physical adsorption.<sup>(7)</sup> The heat of adsorption is several orders of magnitude higher than that found in physical adsorption and is comparable with the energies of chemical bonds. Chemical adsorption is generally not instantaneous, very specific, depending on the chemical nature of both the adsorbent and adsorbate, capable of only monomolecular adsorption, and tends to be irreversibly bound. Because of the characteristics just described, this type of adsorption would be of no use in industrial hygiene sampling as collected contaminants could not be qualitatively or quantitatively analyzed.<sup>(4,6,7,9)</sup>

Any process that tends to decrease the free surface energy (the product of the surface tension and the surface area) occurs spontaneously. A molecule adsorbed by a solid saturates some of the unbalanced forces on the surface and decreases the surface tension. Therefore, all adsorption phenomena (physical or chemical) are spontaneous and result in a decrease of the free energy of the system.<sup>(9)</sup> Adsorption is an exothermic process and the net decrease in

the heat content of the system is defined as the heat of adsorption.<sup>(6)</sup>

Numerous experimental observations have been made concerning the phenomenon of adsorption and have been accepted as fact. In 1814, de Saussure found that for porous adsorbents the most easily condensible gases are adsorbed in the largest quantity. He determined that the volume adsorbed increased as the boiling point of the gas increased. Schmidt found a relationship between the heats of vaporization of gases and their adsorption. All of which correlate van der Waals adsorption with condensation properties of the gases. Recognize however, that there are exceptions to this general rule and realize that the adsorbent may retain a certain affinity for one compound over another. Pearce found a relationship between molecular structure and the amount adsorbed, but it is influenced by the pressure during adsorption.<sup>(4)</sup> At pressures below 1 mm Hg adsorption increases with molecular size in a homologous series while pressures above 1 mm Hg preferentially promotes adsorption of the smaller molecules.<sup>(4)</sup> In accordance with Le Chatelier's principle, the amount of gas adsorbed at equilibrium must always decrease with increasing temperature since adsorption is an exothermic process. Lastly, adsorption also increases with increasing pressure, again relating to the condensibility factor. Therefore, the amount of gas adsorbed at equilibrium is a function of the temperature, pressure, and physical structure and chemical

constitution of the adsorbate and adsorbent. (4,6,7,9)

Extensive research has been conducted on determining the volume of gas adsorbed per unit weight of adsorbent under various environmental conditions. These data are then presented in the form of adsorption isotherms (amount adsorbed at constant temperature and varying pressure), isobars (amount adsorbed at constant pressure and varying temperature), and isosteres (pressure required to maintain constant adsorption at varying temperatures) with the isotherm being the form used almost exclusively because it directly relates to research data. Only five different isotherm types have been identified for van der Waals adsorption for all adsorbents and adsorbates tested.<sup>(9)</sup> After the development of the isotherms, researchers began to formulate theories to explain the observed results. Highlights of the main theories are presented below.

The Freundlich equation, an empirical equation, is the oldest isotherm equation, but is still widely used in industrial practice, particularly in adsorption from liquids because it fits some data very well, although it has limited application in industrial hygiene sampling. It is also referred to as the exponential equation and it should be realized that it is strictly empirical and not based on theory. (6,7,9)

In 1915 Langmuir proposed a theory for adsorption based on a belief that it was a chemical process and that the adsorbed layer was unimolecular. (6,9,10) No far-reaching

forces are envisioned, but when a wandering molecule of vapor collides with a suitable unoccupied surface space, the molecule will adhere.<sup>(4)</sup> Like the Freundlich equation, it has found wide application in the adsorption from liquids.

It is well known that a liquid that wets the walls of a capillary will rise in it with a concave meniscus and the vapor pressure will be lower than in the bulk liquid. In 1911, Zsigmondy studied the uptake of water vapor on silica gel and attributed it to the numerous small capillaries in the gel. He determined that in small capillaries condensation could occur at pressures below the normal vapor pressure. The theory of capillary condensation is based on a stepwise filling of the capillaries. The narrowest capillaries fill at the lowest pressure and as the pressure increases, larger capillaries fill until at the saturation pressure, all the pores of the adsorbent are filled with liquid. Capillary condensation is an important factor when the gas phase pressure approaches the saturation pressure for a porous adsorbent.<sup>(4,6,7,9)</sup>

The Brunauer, Emmett, and Teller (BET) theory was developed in 1938 by applying Langmuir's ideas to multimolecular adsorption. This theory is based on the assumption that the same forces that produce condensation are also responsible for the binding energy of multimolecular adsorption. Its general equation can describe the shape of the five isotherm types throughout the entire range of adsorption which includes unimolecular

adsorption (adsorbate formation of a monolayer), multimolecular adsorption (adsorbate formation of multiple layers), and capillary condensation. Furthermore, it represents the first attempt to arrive at a unified theory of physical adsorption and provides an accurate method for adsorbent surface area determinations.(4,7,9)

The polarization theory was first developed by deBoer and Zwikker in 1929 and is based on adsorption occurring by the induction of dipoles. It has very narrow application as it can explain adsorption of non-polar molecules on ionic adsorbents or polar molecules on non-ionic adsorbents only at conditions not conducive for capillary condensation.(6,9)

The final theory to be discussed is the potential theory developed by Polanyi in 1914. It assumes that adsorption occurs due to long range attractive forces from the surface of the adsorbent and many adsorbed layers can be formed. The layers are under compression, partly from the surface force and partly from the layers adsorbed on top of it. The compression is greatest on the first adsorbed layer where the adsorbate is ascribed liquid-like properties and continually decreases until the last layer which has properties similar to the surrounding gas. It is based on three assumptions: the adsorption potential is independent of the temperature, the potential is independent of the presence of the adsorbate in the space, and under the same conditions, the interaction between adsorbed molecules is the same as that between non-adsorbed molecules. The

adsorption potential is a product to which the surface contributes the same share regardless of what the gas is, and the gas contributes the same share regardless of what the surface is.<sup>(9)</sup> Its significance is that by knowing the affinity coefficient for a given gas on a type I adsorbent, it is possible from a single isotherm to calculate isotherms for this substance at any temperature as well as isotherms for any other substance on the same adsorbent. This theory as modified by Dubinin has been shown to be extremely useful for microporous adsorbents.<sup>(7,9,11)</sup>

#### Adsorption on Activated Charcoal

Langmuir's equation holds for nonporous surfaces where the gas molecules have free access and for adsorbents in which the attraction centers are equal in strength and uniformly distributed over the surface. However, neither of these conditions are applicable to activated charcoal.<sup>(6)</sup> The BET theory proves to be very useful for non-porous and macroporous adsorbents, but breaks down and has serious problems when applied to microporous adsorbents such as activated carbon. Instead, the theory of volume filling of micropores which is based on the potential theory has proven to be best for type I structure adsorbents such as coconut based activated charcoal.<sup>(6,9,11)</sup>

Adsorption consists of three distinct steps: motion of the gas molecules to the surface, movement of the molecules along the surface, and motion of the molecules away from the



surface back to the gas phase (desorption). Adsorption of gases above the critical temperature,  $2/3$  of its boiling point, is unimolecular and the pore structure of the adsorbent is not particularly important; however, adsorption below the critical temperature is multimolecular and the pore structure of the adsorbent plays a vital role. Since most industrial hygiene sampling applications occur below the critical temperature, the pore structure of the carbon adsorbent is critical. In addition, it should be recognized that adsorption on activated charcoal involves mutual affinities between the surface of the carbon and the substance to be adsorbed. (4,9)

The surface of activated charcoal is considered to be heterogeneous, meaning that it consists of randomly distributed sites of varying adsorption potential and is greatly exaggerated by the process of activation. Activated charcoal prepared at temperatures below  $500^{\circ}$  C are more hydrophilic because of acidic surface oxides that are formed. The surface oxides dramatically increase the adsorption of water vapor and other polar molecules as compared to the more basic carbons produced at higher temperatures. (4)

As previously stated, the charcoal activation process increases the surface area available for adsorption by creating numerous pores at the external and internal surface of the charcoal. The pores have been classified by Dubinin into three categories: macropores, mesopores (transitional

pores), and micropores. (6,11)

A macropore is defined as having an effective radius larger than 1000 Angstroms. For typical activated carbons, the effective radius is between 5000 and 20000 Angstroms and their specific surface area does not exceed 2 per cent of the total surface area. Adsorption on the surface is negligible and capillary condensation is unlikely; therefore, macropores function solely in a transport role. (6,11)

A mesopore is defined as having an effective radius of between 20 and 1000 Angstroms and their specific surface area does not exceed 5 per cent of the total surface area. The pore is orders of magnitude larger than the molecule being adsorbed and is filled by capillary condensation. Additionally, they provide further access to the micropores. (6,11)

A micropore is defined as having an effective radius less than 6 or 7 Angstroms and their specific surface area is greater than 95 per cent of the total surface area. The pore is of the same order of magnitude as the molecule being adsorbed and therefore is not filled by capillary condensation but by selective volume filling of the adsorption space. The smallest micropores have the greatest adsorption potential and therefore are filled first at the lowest pressure. As indicated, essentially all of the adsorption occurs in the micropores, but very few of them open to the external surface; so the macro and mesopores are

essential for providing access to the micropores. (6,11)

Once the vapor molecules reach the external surface of activated charcoal they can proceed to the internal surface by four different mechanisms: by diffusion in the pores, by surface diffusion, by viscous flow in the adsorbed phase through the transfer of capillary-condensed adsorbate, or by the action of capillary forces. (6) Transport within the macropores is through convective flow and diffusion in the pores, while transport within the meso and micropores is through surface diffusion. (6)

#### Charcoal Tubes

Charcoal tubes are used extensively in the application of industrial hygiene. In fact, the validated sample collection method for many organic compounds is based on drawing a known volume of air, via a pump, at a constant flow rate of between 10 and 200 ml/min through a charcoal tube. (12) The pump must be calibrated prior to and immediately following any sampling event to ensure the proper flow rate was maintained. The standard charcoal tube contains approximately 100 mg of activated charcoal in a front section and 50 mg in a back-up section. The activated charcoal is a 20/40 mesh and generally coconut based. The surface area of SKC 20/40 mesh charcoal is between 1150 - 1250 m<sup>2</sup>/gm with ninety-nine percent of the internal surface area associated with micropores. (13) The function of the back-up section is to collect any of the substance, which

because of contaminant loading, was not collected on the front section. This enables the industrial hygienist to determine if significant breakthrough has occurred and if the sample needs to be recollected. Breakthrough is defined as the back-up section concentration being 10% of the front section concentration.

NIOSH developed the Manual of Analytical Methods<sup>(12)</sup> which provides a listing of the validated methods for collection and analysis of many chemical and biological agents. It also includes the sampling flowrate ranges, minimum and maximum sampling volumes, and desorption solvent and method.

#### Relative Humidity Effects

Much research has been performed to determine what effect relative humidity has on the adsorption of vapors on activated charcoal.<sup>(2,3,14-31)</sup> Generally, the increased water vapor causes capillary condensation within the micropores and reduces the number of sites for active adsorption.<sup>(2)</sup>

Werner investigated the effect of relative humidity, varying between 5 and 85%, on activated carbon adsorption of trichloroethylene (TCE). A dynamic solvent evaporation sampling system consisting of three separate air streams for solvent laden, water vapor laden, and dry dilution air was employed. The air streams were mixed in a 20-liter equalization vessel after which temperature and dew point

measurements were obtained and a hygrocomputer determined the relative humidity. The test stream was split with one portion diverted to a gas chromatograph for influent TCE concentration determination, while the rest was directed through the 37.5 gram and 13.5 cm activated carbon column. Results indicated that the amount of TCE adsorbed decreased with increasing relative humidity. Note however, at least four factors influence the impact of humidity on adsorption: carbon preconditioning, solvent concentration, adsorbate compound, and type of activated carbon. Furthermore, each set of data fit the Dubinin-Polanyi equation indicating its usefulness for predicting the effect of humidity on gaseous phase carbon adsorption. The author also concluded that relative humidity levels below 50% can adversely impact the adsorption process depending on the adsorbate concentration. (14)

Rudling and Bjorkholm investigated the effect of adsorbed water on solvent desorption of vapors collected on activated carbon. In this study, two types of activated charcoal, Merk and SKC, were loaded with water prior to syringe injection of the desired solvent contaminant. Desorption efficiencies were then calculated using both polar and non-polar solvents. The charcoal adsorbents were of equal surface area but the Merk contained acidic surface oxides and the SKC contained basic surface oxides. The results indicated a number of things: charcoal with acidic surface oxides adsorb more water at lower relative

humidities; compounds which are insoluble in water are not affected much by adsorbed water; the effects caused by 20-30% relative humidity vary between both compounds and adsorbents; and the highest humidity, 80%, caused a decrease in desorption efficiency for all water soluble compounds and adsorbents. The authors concluded that at high humidities desorption efficiency was not affected for water soluble compounds desorbed with polar solvents, and at high humidities desorption efficiency was decreased for water soluble compounds desorbed with non-polar solvents. The decreased efficiency depends on the amount of water adsorbed and the distribution ratio of water/carbon disulfide.<sup>(2)</sup>

Gregory and Elia investigated the effects of contaminant concentration, relative humidity, competitive solvent, and zero solvent exposure period on the retention of vapors adsorbed on passive dosimeters and charcoal tubes. In the study, a dynamic solvent evaporation sampling system was used to load the samplers with a solvent after which they were exposed to periods of zero contaminant concentration with varying humidity levels. The results showed that significant sample loss in the charcoal tube occurred only for methyl chloroform at the highest humidity (70%) and longest time with (3hr) and without (6hr) use of toluene as a competitive solvent. However, significant sample loss in the passive dosimeters occurred for methyl chloroform, methylene chloride, and isopropanol at the highest humidity regardless of the length of time and

competetive solvent. In addition, sample losses can be substantially reduced by lowering the sampling rate. The authors concluded that significant sample loss occurs only for compounds that are highly volatile and weakly adsorbed onto activated charcoal.(15)

Jonas et al investigated the effect of relative humidity on the adsorption of chloroform by activated carbon. Three different environmental conditions were examined: chloroform and water vapor were introduced concurrently into a dry carbon bed, dry chloroform was introduced into a humidified carbon bed, and humidified chloroform was introduced into a carbon bed at the same relative humidity. The carbon bed was made out of 2.25 grams of a 6-10 mesh activated charcoal. The results clearly indicated that the carbon beds pre-humidified above 50% relative humidity had significantly lower breakthrough times. The authors concluded that adsorption of a vapor soluble in water but not hydrolyzed by it should be relatively unaffected by relative humidity. However, a vapor insoluble in water should be increasingly affected with increasing relative humidity.(16)

Andersson et al studied the effect of varying relative humidity on the sampling efficiency of several different types of solid adsorbents including activated charcoal. The humidity levels were generated dynamically by passing air through a glass bubbler filled with water while solvent concentrations were generated statically through liquid

injection with evaporation. Twelve different compounds were tested, ranging in polarity from highly polar ethylene glycol to nonpolar naphthalene. The results showed that the collection efficiency on activated charcoal was decreased only for the most polar compound at the highest humidity (85%).<sup>(17)</sup>

Hall et al studied the effect of water vapor on the Wheeler kinetic model. The Wheeler model has showed the most promise for use as a predictor of respirator performance. The adsorbent used was a standard respirator cartridge with 1.2 grams of a 12-20 mesh petroleum-based granular activated charcoal and the adsorbates were carbon tetrachloride and triple distilled water. The results clearly indicated that relative humidity levels in excess of 50% decreased both the adsorption rate constant and the kinetic adsorption capacity parameters for the Wheeler model. As the system water vapor concentration was increased, the adsorption capacity showed a decrease which was linear when plotted against % relative humidity.<sup>(18)</sup> The predicted minimum capacity at fully saturated conditions represented a 45% reduction from the dry carbon value. Therefore, predictions based upon dry carbon values would severely overestimate the protective capacity of a respirator adsorbent cartridge. Realize however, that this data represents the worst case, a cartridge fully saturated with water vapor and an adsorbate with poor water solubility.<sup>(18)</sup>



Wood investigated the effect varying levels of relative humidity had on the adsorption capacities of charcoal beds. The purpose of the study was to develop a model that could be used to predict the effect of humidity. The charcoal beds were preconditioned at the same relative humidity that they would be tested under. The results showed that the model successfully describes the effect of relative humidity on decreasing breakthrough times of water-immiscible adsorbates on activated charcoals. The author concluded that the data was very limited and more was needed to determine the model's limitations such as does it hold for water-soluble vapors. (19)

Okazaki et al proposed a new prediction equation for binary adsorption of solvent and water vapor on activated carbon. The experimental results were then compared with the predicted value to determine the validity of the proposed model. The model assumes that water vapor adsorption occurs by capillary condensation and solvent adsorption occurs by a combination of vapor-phase adsorption onto the dry surface, dissolution of the solvent from the gas phase into the condensed phase, and liquid-phase adsorption onto the wet surface. This implies that a pore critical radius exists, below which capillary condensation occurs and above which it does not. In the experiment, both water-soluble solvents, acetone and methanol, and water-insoluble solvents, benzene and toluene, were used along with two different types of activated charcoal. The results

showed good agreement between the predicted and observed values but the predicted amount of water vapor adsorbed was always lower than that observed. The data necessary for prediction are the single-component isotherms, the liquid-phase isotherms, and the isothermal vapor-liquid equilibria. (20)

Crittenden et al examined the effect of relative humidity and competitive solvent for gas-phase adsorption on granular activated carbon (GAC). The research goal was to formulate a prediction model capable of determining GAC utilization in treatment of air stripping off-gas. The Dubinin-Radushkevich equation was used to predict single component adsorption while Okazaki's model was used to predict single component adsorption in the presence of water vapor. Multicomponent equilibria were predicted using the Polanyi potential theory and the ideal adsorbed solution theory (IAST). The low organic vapor concentrations and humidities that were examined are similar to those that would be encountered in air stripping tower air emissions. (23) The results indicated that all four models gave an accurate prediction for adsorption on GAC. The data required to predict the single-component adsorption equilibria are a reference isotherm for the exact GAC utilized and the physical properties of the adsorbate, while for binary adsorption equilibria the single-component isotherm for the adsorbates being used is sufficient. (21-23)

Rushlow researched the effect of pre-exposure to

relative humidity on the collection efficiency of charcoal tubes and passive dosimeters for competitive solvent vapors. Sets of both samplers were exposed to a contaminant-free humidified atmosphere for two hours followed by an equal acetone-toluene contaminant mixture with humidity for two more hours. Results indicated a significant reduction in collection efficiency for both sampling methods of all vapors at levels of 50% and 80% relative humidities. Furthermore, the collection efficiency for the more polar compound acetone was significantly lower than that for toluene. Note however, that the competitive solvent effect was not differentiated from the relative humidity effect on the collection efficiency.<sup>(3)</sup>

Several additional prediction models for activated carbon adsorption of vapor mixtures were examined and are now summarized.<sup>(24-26)</sup> All authors recommended using the Dubinin-Radushkevich equation but differed in their calculation methods. Urano suggested that the affinity coefficient for adsorption on activated charcoal could be approximated by the ratio of molar volumes ( $V/V_s$ ) or parachors ( $P/P_s$ ) of an adsorbate to the standard adsorbate regardless of the type of activated carbon; however, for polar adsorbates the ratio of polarities gave a better approximation.<sup>(24)</sup> Jonas recommended that the adsorption behavior of mixtures could be predicted when the vapor concentrations were expressed in terms of their mole fraction.<sup>(25)</sup>

### Concentration Effects

Underhill expanded the Dubinin-Radushkevich equation to account for the effect of relative humidity during adsorption on activated charcoal. He concluded that the effect of relative humidity is more severe at lower rather than higher concentrations of contaminant. (27)

Wood developed a model to describe relative humidity effects on adsorption capacities of water-immiscible vapors. The model has been demonstrated to be applicable for vapor concentration effects as well. The author concluded that at higher relative humidities, dry charcoal beds are heated significantly by the adsorption of water vapor which affects the capacity and other physiochemical characteristics of the adsorbent. Additionally, model parameters can be used for comparisons of charcoal characteristics, adsorbate-charcoal interactions and water-charcoal interactions. (28)

Nelson and Harder investigated the effect of relative humidity and adsorbate concentration on the service life of organic vapor respirator cartridges. They observed no significant difference in cartridge service life between steady-state and pulsating flow indicating that the adsorption kinetics are practically instantaneous. In addition, the amount of solvent adsorbed at a given temperature, humidity and concentration is essentially constant and is independent of the flow rate associated with normal breathing. The results showed that within each

homologous series of chemicals the most volatile solvent breaks through first. The authors concluded that activated carbon has a greater affinity for the less volatile materials and that relative humidity significantly decreased activated carbon's affinity for water-soluble solvents.(29)

Two articles previously reviewed in the humidity section also reported adsorbate concentration effects. Werner showed that the effect of humidity was more pronounced for the lower TCE concentrations.(14)

Jonas et al showed that as the benzene concentration in the vapor-air mixture decreased there was a progressive increase in the effect of moisture on benzene adsorption, They concluded that it was caused by the reduced localized heat of adsorption which displaced less of the adsorbed moisture.(16)

#### Polarity Effects

The effect of a substituent group on adsorption is often associated with changes in other properties and this can lead to seeming inconsistencies. A polar group such as  $-OH$  will decrease the adsorption from a solution because it becomes more water soluble, but the same polar group will increase the adsorption of a vapor because it becomes more condensable.(4)

Rudling studied the effect of mixtures of polar solvents on desorption efficiency from activated carbon. Four binary mixtures were prepared in hexane and added to

100 mg of oven dried SKC lot 120 activated charcoal. The results indicated that a vapor with a high affinity for the activated carbon can displace vapors with a lower affinity. An increased recovery for butanol occurred when 2-ethoxyethanol was present in the mixture; however, dioxane in the mixture did not increase recovery. This is what would be expected based on the electron donor-acceptor strength of these compounds. The presence of nonpolar solvents doesn't influence the results because they are not adsorbed on the hydrophilic surface oxide sites. The author concluded that an increased desorption efficiency can be obtained for polar solvents adsorbed on activated carbon when present in mixtures.<sup>(30)</sup>

In other literature reviewed, White reported that polar compounds tend to be displaced from the front section to the back-up section of a charcoal tube when sampled in the presence of high concentrations of nonpolar organic solvents. In general, 25 % of the polar solvent was displaced independent of the sampling rate.<sup>(31)</sup> Muller and Miller reported that a definite increase in desorption efficiency is obtained when mixtures of polar compounds are treated together rather than individually. The increased efficiency suggests that a certain number of polar molecules are irreversibly sorbed, and the amount retained is a function of available active sites, which reinforces the postulate that polar species compete for active sites on charcoal to give overall higher efficiencies for all polar

compounds present in a mixture.<sup>(1)</sup>

### The Problem

High levels of relative humidity have been shown to adversely affect the adsorption process on activated charcoal; however, much of the research has been centered around its negative effect on breakthrough times in packed carbon beds and respirator cartridges. In fact, some accurate prediction models have been developed but they do not help determine the effect of humidity on charcoal tubes. Some additional research has shown that the effect of humidity is more pronounced for polar than non-polar compounds, but no literature is available correlating polarity or water solubility of adsorbates with the reduced collection efficiency. Therefore, this research was undertaken to correlate the effect of compound type and humidity on collection efficiency. This will be accomplished by exposing tubes to relative humidity for two hours prior to a two hour combined humidity and contaminant exposure for a total exposure of four hours for four different compounds.

## METHODOLOGY

### Overview

This experiment consisted of exposing charcoal tubes to room air, passed through a dryrite/activated charcoal canister to ensure it was free of contaminants, at set relative humidity levels for a period of time followed by single solvent contaminant exposure at the same relative humidity for an identical period of time. The experiment was designed to determine if a correlation existed between humidity effects on collection efficiency and the contaminant's polarity or water solubility.

### Contaminants

The compounds, ethyl ether, ethyl acetate, 1-propanol, and 2-methoxyethanol, investigated were all oxygenated hydrocarbons with varying polarities and water solubilities. They were selected based on molecular structure and weight similarities, adequate vapor pressures ensuring volatilization, and polarity and water solubility factors. All four compounds are readily adsorbed on activated charcoal and easily recovered. In addition, they all have a validated sampling and analysis method approved by NIOSH. Appendix A lists some of the physical and chemical characteristics for the four compounds.



### Sampling Devices

SKC Lot # 120 charcoal tubes utilizing 20/40 mesh coconut based activated charcoal were used to conduct all adsorption experiments. A charcoal tube contains approximately 100 mg of charcoal in a front section which is then separated via a plug from a 50 mg back-up section. Both sections were analyzed to ensure contaminant breakthrough did not occur and obtain complete and accurate measurement of the adsorption process.

MDA 808 Accuhaler pumps were used to initiate the sampling regime. It is a motor driven diaphragm actuated pump which operates by drawing a constant volume per stroke. The actual sampling rate of the pump is varied by changing the sampling orifice such that the area will allow the volume to be drawn within a specific time interval. In this particular experiment, an orifice was used that gave an approximate sampling flow rate of 20 ml/min.

### Contaminant and Water Vapor Generation

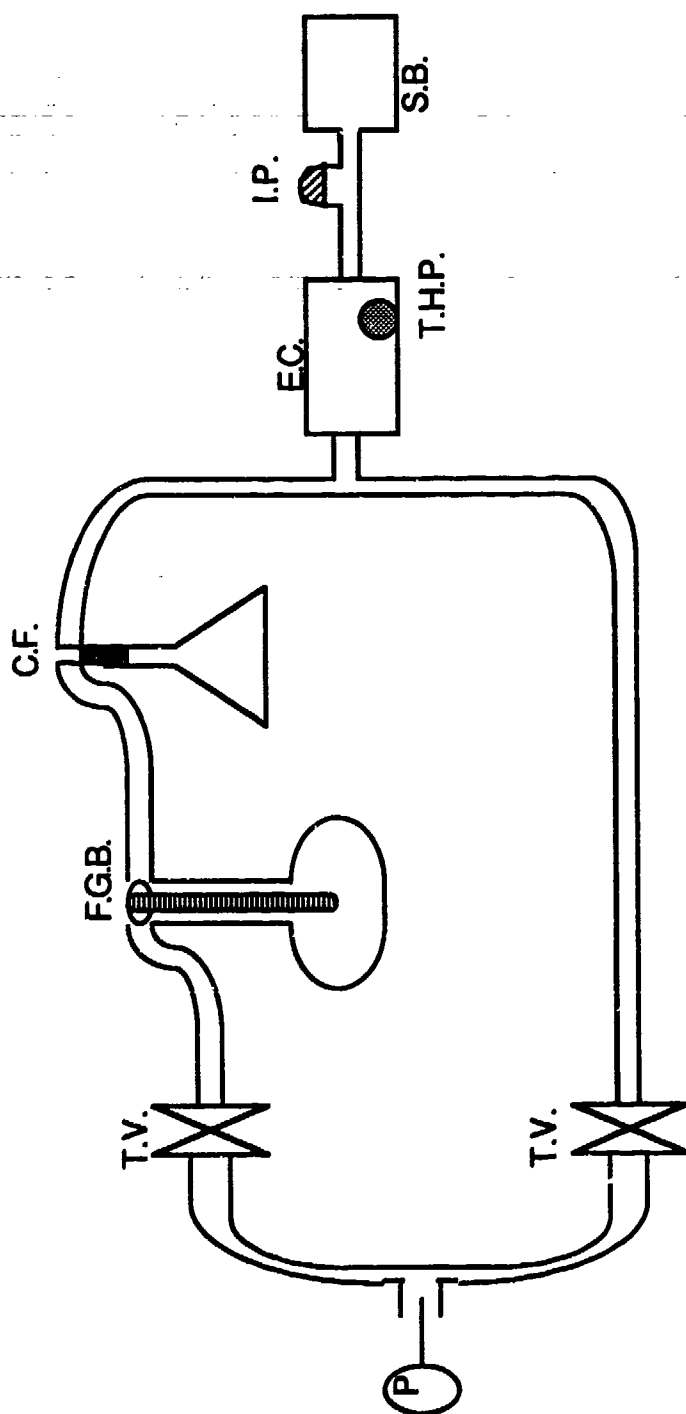
Only reagent grade ethyl ether, ethyl acetate, 1-propanol, and 2-methoxyethanol were used in this research project. The steady state contaminant concentration levels were produced using a static contaminant generation system.<sup>(32)</sup> A predetermined volume of air was pumped into a sealed Tedlar bag. During the filling process, a calculated amount of liquid solvent was injected and vaporized into the air stream via a heated and packed injection port. Appendix

B contains all information necessary for calculating the amount of liquid solvent required as well as a sample calculation.

A dynamic system was used to produce the desired humidity concentrations.<sup>(32)</sup> A General Electric centrifical pump Model No. 5KH1066R285 provided the room air which was dehumidified and cleaned by passing through a canister containing drierite and activated charcoal. The air stream was split with one portion being passed through a water evaporation apparatus using a fritted glass bubbler device and the other portion being used for dry dilution air. The humidified air stream was passed through a glass flask to remove any condensation prior to mixing with the dilution stream. The re-mixed stream was directed into an exposure chamber constructed for a pervious research project (Figure 1). A General Eastern Model 400E Relative Humidity and Temperature Indicator was placed in the chamber allowing continuous monitoring of humidity and temperature. After the exposure chamber came to equilibrium and the desired humidity was reached, the effluent from the chamber was used to fill the sampling bags.

#### Sampling Bag

As previously stated, sealed Tedlar sampling bags were used to generate the static sampling atmosphere. A 24 hour leak test was performed to assure the integrity of the bags selected for the experiment. Furthermore, a contaminant



P = Pump	E.C. = Equalization Chamber
T.V. = Throttling Valve	I.P. = Injection Port
F.G.B. = Fritted Glass Bubbler	T.H.P. = Temperature & Humidity Probe
C.F. = Condensation Flask	S.B. = Sampling Bag

NOTE: Diagram is not drawn to scale.

Figure 1. Schematic Diagram of Experimental Set-up

leakage test was performed to ensure that none of the four solvents readily penetrated the bag. Two sampling bags were filled with identical solvent concentrations; however, one was sampled immediately with a charcoal tube while the other was sampled after a two hour waiting period. This procedure was repeated for each of the four different solvents and the results indicate that significant leakage did not occur for any of the solvents.

#### Experimental Procedure

Six sampling bags which passed the testing conditions were selected, numbered, and grouped with a specific MDA 808 Accuhaler pump so bag and pump variations could be investigated. The pumps were pre-calibrated and post-calibrated in accordance with manufacture's instruction and fitted with the appropriate orifice to sample at a flow rate of approximately 20 ml/min.

The experiment consisted of four separate contaminant compounds; ethyl ether, ethyl acetate, 1-propanol, and 2-methoxyethanol, sampled at two different levels for both humidity, 50% and 80%, and solvent concentration, 50 ppm and 200 ppm. A sample run required four hours of exposure broken down into two, two hour sub-sets. The initial two hour sampling period required a steady state relative humidity level with zero contaminant exposure. The final two hour sampling period required an identical humidity level with contaminant exposure.

For each contaminant vapor investigated, four separate samples were required, but each sample was repeated in triplicate equaling a total of twelve samples. Since each run contained six samples, a contaminant gas could be completely quantified with two runs. All sample parameters were randomized as much as practical; however, once the contaminant and humidity level were chosen they remained constant for the entire run. Table I is an example of the sampling parameters for each run and the complete data is contained in Appendix C.

As previously stated, the effluent from the exposure chamber was used to fill the sampling bags. During the second sub-set, the quantity of air placed in the sampling bag must be exact in order to obtain the required contaminant concentration. Therefore, a Gilibrator was used to determine the exact flow rate out of the chamber from which the bag filling time could be calculated. The initial and final humidity as well as initial and final temperature readings were recorded during bag filling and the average value reported. Appendix D contains the sampling information sheets.

A predetermined amount of liquid solvent was injected while filling the gas sampling bag with six liters of humidified air from the exposure chamber. All samples were initiated from within the bag using constant volume air flow pumps and collected on SKC charcoal tubes. Sample volumes and concentrations were corrected to standard temperature

TABLE I

## Sampling Parameters for a Run

Bag #	Vapor	Relative Humidity %	Approximate Concentration ppm	Total Vol Liters
1	Ethyl Ether	80	200	4.90
2	"	80	50	4.66
3	"	80	200	3.91
4	"	80	200	4.24
5	"	80	50	3.83
6	"	80	50	4.60
1	Ethyl Ether	50	50	4.91
2	"	50	200	4.68
3	"	50	50	3.91
4	"	49	200	4.24
5	"	49	200	3.08
6	"	50	50	4.61

and pressure. All samples were desorbed in accordance with standard NIOSH analytical methods. Actual contaminant concentrations were determined through gas chromatographic analysis.

### Analysis

Sample analysis was conducted in accordance with the NIOSH Methods 1610, 1450, 1401, 1403 for ethyl ether, ethyl acetate, 1-propanol, and 2-methoxyethanol respectively. After collection, the samples were capped and stored in a freezer maintained at a temperature of  $-5^{\circ}\text{C}$  until they were desorbed. All of the samples were analyzed within two weeks of exposure. The charcoal tube was separated into two glass vials, one for the 100 mg front section and one for the 50 mg back-up section. One milliliter of the required desorbing solvent was mixed with each vial and shaken in a SKC Charcoal Developer for one half hour to assure complete desorption. As required, two blanks and five calibration injections were made for each run to ensure the integrity of the charcoal and gas chromatograph.

All samples were analyzed by a Varian 3400 Gas Chromatograph (GC) utilizing a flame ionization detector (FID). A sample injected into the GC will partition itself between a carrier gas (helium) and a stationary phase (column) and is separated into individual components. The components are then moved by the carrier gas to the FID and ionized. The charged molecules which are formed results in

a decrease in the resistance and increase in the current. This current is then directed to a stripchart recorder.<sup>(3)</sup>

After the desorption step was completed, four one-microliter samples were injected into the GC. The first determined the best attenuation for that particular sample and the other three were used to obtain an average reading. New calibration standards were made each day and a calibration curve was generated each day. Appendix E contains the calibration curves.

The values obtained from the compound-specific calibration curve were divided by the corresponding experimentally determined desorption efficiency to obtain the actual amount of contaminant originally adsorbed. Appendix F contains all information related to desorption efficiency determinations.



## RESULTS AND DISCUSSION

The average GC peak heights and other factors used in calculating the concentrations for each run are presented in Appendix G. A summary of the resulting collection efficiencies are presented in Tables II through V. Initial inspection of Tables II, IV, and V show a tendency to decrease in collection efficiency with increasing relative humidity while Tables III, IV, and V show a tendency to decrease in collection efficiency with decreasing contaminant concentration. In addition, comparison of Tables II through V indicate compound type also influences collection efficiency. Note however, that most of the collection efficiencies for ether were above one, which is unusual, but may be explained by the extremely low desorption efficiency obtained during analysis. The average NIOSH desorption efficiency is 0.98 in comparison to 0.84 for this research project.

Previous research has shown that relative humidity, contaminant concentration, and compound type affect the collection efficiency on charcoal tubes. Therefore, the following statistical model was proposed:

$$Y_{ijk} = U + H_i + C_j + T_k + H_i * C_j + H_i * T_k + C_j * T_k + H_i * C_j * T_k + E_{ijk}$$

Where:

$Y_{ijk}$  = Collection efficiency response variable.

TABLE II

## Collection Efficiencies for Ethyl Ether

Collection Efficiency	Humidity %	Approximate Concentration ppm
1.40	50	50
1.33	50	50
1.30	50	50
1.01	50	200
1.07	49	200
1.11	50	200
1.13	80	50
1.21	81	50
1.04	80	50
1.00	80	200
1.01	80	200
0.99	80	200

TABLE III

## Collection Efficiencies for Ethyl Acetate

Collection Efficiency	Humidity %	Approximate Concentration ppm
0.36	51	50
0.38	51	50
0.32	51	50
0.69	50	200
0.69	50	200
0.64	51	200
0.48	80	50
0.42	80	50
0.45	80	50
0.72	79	200
0.67	79	200
0.70	79	200

TABLE IV

## Collection Efficiencies for 2-Methoxyethanol

Collection Efficiency	Humidity %	Approximate Concentration ppm
0.47	49	50
0.46	50	50
0.46	50	50
0.59	50	200
0.59	50	200
0.53	50	200
0.41	80	50
0.42	80	50
0.41	80	50
0.68	80	200
0.67	80	200
0.64	80	200

TABLE V

## Collection Efficiencies for Propanol

Collection Efficiency	Humidity %	Approximate Concentration ppm
0.52	49	50
0.57	50	50
0.54	50	50
0.62	50	200
0.63	50	200
0.62	50	200
0.34	80	50
0.39	80	50
0.35	81	50
0.42	80	200
0.44	80	200
0.42	80	200

$U$  = Overall mean.

$H_i$  = Effect due to humidity  $i = 1, 2$ .

$C_j$  = Effect due to concentration  $j = 1, 2$ .

$T_k$  = Effect due to compound type  $k = 1, 2, 3, 4$ .

$H_i * C_j$  = Interaction between treatments H and C.

$H_i * T_k$  = Interaction between treatments H and T.

$C_j * T_k$  = Interaction between treatments C and T.

$H_i * C_j * T_k$  = Interaction between treatments H, C, and T.

$E_{ijk}$  = Random error associated with the response for treatments H, C, and T.

The statistical analysis software (SAS) package was used to perform all statistical analyses. An analysis of variance (ANOVA) test utilizing general linear models (GLM) was conducted to determine if any of the proposed model treatments had a statistically significant effect on collection efficiency at the 0.05 level of significance. All of the necessary SAS output is contained in Appendix H.

The analysis clearly showed that sampling instrumentation did not affect the results as the p-value was extremely high 0.7746. However, all three of the proposed main effects; humidity, concentration, and compound type were highly significant with p-values of less than 0.0001. In addition, significant interaction did occur between all three treatment variables with p-values ranging from less than 0.0001 to 0.0136. Overall, the proposed model appeared to fit the data excellently as it gave an  $R^2$

value of 0.991.

However, due to the significant three-way interaction between the main effects, an additional analysis was performed. The collected data was separated by compounds (See Tables VI and VII) and then an ANOVA test using GLMs was conducted to interpret the interaction. This was followed by the Protected Fisher Least Significant Difference (LSD) test to determine if significant pairwise differences in mean collection efficiency between the treatment groups occurred.

These results indicated that all means for all treatments at both levels were significantly different from each other. Significant interaction between humidity and concentration only occurred for the highly polar, doubly oxygenated compound 2-Methoxyethanol.

#### Ethyl Ether:

The results showed that both treatments were highly significant (p value .0002). As the humidity increased the collection efficiency significantly decreased at both concentration levels which is as expected. However, as the concentration increased, the collection efficiency significantly decreased at both humidity levels which is exactly opposite of what was expected (Refer to Table VI).

#### Ethyl Acetate:

The results showed that both treatments were highly significant (p value .0001). For this case, the concentration effect was as expected, as concentration

TABLE VI

## Mean Collection Efficiencies (Ether and Acetate)

## ETHYL ETHER

C o n c e n t r a t i o n	Humidity %		
	50	80	
	50 ppm	1.34	1.13 D
	200 ppm	1.15	1.00 D
	LSD = .1052	D	D
	MSE = .00312		
	CV = 4.93		

## ETHYL ACETATE

C o n c e n t r a t i o n	Humidity %		
	50	80	
	50 ppm	0.35	0.45 I
	200 ppm	0.67	0.70 I
	LSD = .0526	I	I
	MSE = .00078		
	CV = 5.15		

D = Decrease

I = Increase



TABLE VII

Mean Collection Efficiencies (2-Methoxy and Propanol)

2-METHOXYETHANOL				
C o n c e n t r a t i o n			Humidity %	
			50	80
	50 ppm		0.46	0.41 D
	200 ppm		0.57	0.66 I
	LSD = .04147	I	I	
	MSE = .00049			
	Cv = 4.17			
PROPANOL				
C o n c e n t r a t i o n			Humidity %	
			50	80
	50 ppm		0.54	0.36 D
	200 ppm		0.62	0.43 D
	LSD = .0397	I	I	
	MSE = .00044			
	Cv = 4.31			

D = Decrease

I = Increase

increased so did the collection efficiency. However, as the humidity increased so did the collection efficiency which is again exactly opposite from what was expected (Refer to Table VI).

#### 2-Methoxyethanol:

The results showed that only concentration and the interaction term were significant (p value .0001). Again, the concentration effect was as expected, but the significant interaction became apparent in the humidity results. Increasing the humidity caused a decrease in collection efficiency at the low concentration, but at the same time caused an increase in collection efficiency at the high concentration (Refer to Table VII). Actually, humidity caused significant differences at both levels, but since they were exactly opposite, when they were averaged the result was not significant.

#### Propanol:

The results showed that both treatments were highly significant (p value 0.0001). Both results were as expected, increasing concentration caused an increase in collection efficiency while increasing humidity caused a decrease in collection efficiency (Refer to Table VII).

Initial inspection of Tables VI and VII may indicate that the assumption of equal variances does not hold (Ether MSE=.003); however, ether had a much higher mean, and closer inspection of the coefficient of variance shows that the variances are indeed similar.

The results presented are consistent with previously documented research. Relative humidity levels of 50 % and above seriously affect collection efficiency with a greater effect caused by increasing levels of humidity. (2,3,14-16,19,27,28) The contaminant concentration effect was identical to Werner's findings. (14) Decreasing levels of contaminant concentration caused an exaggerated relative humidity effect, further reducing the collection efficiency. Previous research on the contaminant compound effect has generated mixed results. Werner and others (14,16) indicated that the more hydrophobic compounds are affected to a greater extent by humidity while Andersson and others (2,17) indicated just the opposite, hydrophilic compounds are more greatly affected. The results from this research support the conclusion that hydrophilic compounds are significantly more affected by relative humidity. The two most polar compounds, propanol and 2-methoxyethanol, had the lowest mean collection efficiencies with propanol being statistically lower from all of the others. Ethyl ether on the other hand was the least polar and had the highest mean collection efficiency. The reduction in collection efficiency due to increasing compound polarity can be satisfactorily explained by the examination of the effects of polarity on desorption efficiencies. Rudling and Bjorkholm showed that desorption efficiencies for polar compounds adsorbed on activated charcoal in the presence of water were reduced. (2) It is the further reduction in the

desorption efficiency that is responsible for the additional loss in collection efficiency.

As previously stated, the ether results were suspect because the collection efficiencies indicated a collection of over 100 % and the concentration effects were exactly opposite of the other three compounds. As a result, identical statistical analyses were performed on the data set excluding ether, resulting in identical conclusions to those found in the set including ether.

## CONCLUSIONS AND RECOMMENDATIONS

The results clearly indicate that humidity, contaminant concentration, and compound type seriously impact the adsorption of vapors on activated charcoal. For this kind of research, the most commonly investigated effect is the resulting collection efficiency. In this particular case, it was decreased by 30 to 60 % depending on the combination of levels of the three influencing factors which is very significant even though interaction between all variables occurred. Keep in mind interaction just indicates that the resulting changes in mean collection efficiency from one treatment level to the next level is not the same across a second treatment factor. Humidity is by far the most influencing factor in determining the reduction in collection efficiency but its effect can be exaggerated or limited by contaminant concentration and compound type. Note that collection efficiency implies an inability of the charcoal tube to adsorb all of the contaminant vapor present; however, none of the samples showed contaminant breakthrough. It is believed, therefore, that the reduced collection efficiency is a result of the effect of water interference with the desorption procedure and not from adsorbed water vapor decreasing the adsorption capacity of the charcoal. This would also explain the concentration effect noticed. The higher contaminant concentrations would reduce the amount of water vapor adsorbed which would reduce

the desorption effect. This forms the basis for recommended future research.

First, a project similar to this one but with only one highly polar compound at three different humidity levels and four different concentrations should be run; however, the procedure for determining the desorption efficiency should be modified. Two sets of DEs should be run, both by the standard NIOSH method but one set should use tubes previously exposed to 80 % relative humidity. The expected result would show a significant difference between the two desorption efficiency methods. The humidified tubes should have a much lower efficiency and may account entirely for the loss in sample collection efficiency.

Second, a project should be undertaken that could investigate the interactive effect between relative humidity and concentration. It should include at least four different humidity levels at four different concentrations.

Lastly, a project examining the effect of humidity on different types of activated charcoal should be conducted. The parameters of the Polanyi-Dubinin equation should be determined ahead of time and the results compared to the predicted equation.

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**APPENDIX A**

Chemical and Physical Properties of Contaminant Solvents<sup>(33)</sup>

	Ethyl Ether	Ethyl Acetate
Formula	$C_6H_{10}O$	$C_4H_8O_2$
Molecular Weight	74.12	88.11
Density @ 20°C	0.7133	0.9006
Boiling Point (°C)	34.55	77.1
Vapor Pressure @ 20°C (Torr)	442	73.0
Polarity Index	2.8	4.4
Solubility in Water @ 20°C	6.89%	8.7%

	Propanol	2-Methoxyethanol
Formula	$C_3H_8O$	$C_3H_8O_2$
Molecular Weight	60.09	76.10
Density @ 20°C	0.8037	0.9646
Boiling Point (°C)	97.2	124.6
Vapor Pressure @ 20°C (Torr)	14.5	9.7
Polarity Index	4.0	5.5
Solubility in Water @ 20°C	Miscible in all Proportions	Miscible in all Proportions

**APPENDIX B**

### Contaminant Concentration Generation

Temperature:	19.1 °C
Barometric Pressure:	762.22 mm Hg
Flow Rate:	3.57 lit/min
Time:	1 min 41 sec
Total Volume:	6.0 lit
Solvent:	Ethyl Ether
Density:	0.7133
Molecular Weight:	74.12
Contaminant Concentration:	200 ppm

#### SAMPLE CALCULATION:

$$\begin{aligned}
 X \text{ ul} &= \frac{(\text{Conc ppm}) (\text{MW}) (\text{Vol}) (273/\text{Temp}) (\text{Bar Press}/760)}{(1 \times 10^{-3}) (\text{Density}) (22.4) (1 \times 10^6)} \\
 X &= \frac{(200) (74.12) (6) (273/292.1) (762.22/760)}{(1 \times 10^3) (0.7133) (22.4)} \\
 X &= 5.2 \text{ ul}
 \end{aligned}$$

**APPENDIX C**

TABLE C1

## Sampling Parameters For A Run

Bag #	Vapor	Relative Humidity %	Approximate Concentration ppm	Total Vol Liters
1	Ether	80	200	4.90
2	"	80	50	4.66
3	"	80	200	3.91
4	"	80	200	4.24
5	"	80	50	3.83
6	"	80	50	4.60
1	Ether	50	50	4.91
2	"	50	200	4.68
3	"	50	50	3.91
4	"	49	200	4.24
5	"	49	200	3.08
6	"	50	50	4.61

TABLE C2

## Sampling Parameters For A Run

Bag #	Vapor	Relative Humidity %	Approximate Concentration ppm	Total Vol Liters
1	Acetate	50	50	4.81
2	"	50	50	4.65
3	"	50	50	4.07
4	"	50	200	4.18
5	"	50	200	4.30
6	"	50	200	4.40
1	Acetate	80	200	5.02
2	"	80	50	4.83
3	"	80	200	3.18
4	"	80	50	4.27
5	"	80	50	4.52
6	"	80	200	4.58



TABLE C3

## Sampling Parameters For A Run

Bag #	Vapor	Relative Humidity %	Approximate Concentration ppm	Total Vol Liters
1	Propanol	80	200	4.82
2	"	80	200	4.57
3	"	80	50	3.88
4	"	80	50	4.17
5	"	80	50	3.86
6	"	80	200	4.48
1	Propanol	49	50	4.78
2	"	50	200	4.52
3	"	50	50	3.80
4	"	50	50	4.12
5	"	50	200	3.74
6	"	50	200	4.47

TABLE C4

## Sampling Parameters For A Run

Bag #	Vapor	Relative Humidity %	Approximate Concentration ppm	Total Vol Liters
1	2-Methoxy	49	50	4.78
2	"	50	200	4.51
3	"	50	50	3.87
4	"	50	200	4.26
5	"	50	200	4.15
6	"	50	50	4.49
1	2-Methoxy	80	200	4.75
2	"	80	200	4.48
3	"	80	50	3.79
4	"	80	200	4.16
5	"	80	50	4.26
6	"	80	50	4.45

**APPENDIX D**





**APPENDIX E**

## CALIBRATION DATA

## Ethyl Ether

Conc	Peak Hgt		Regression Output:
0.29	8		
0.96	24	Constant	0.074958
2.89	70	Std Err of Y Est	0.101219
4.82	123	R Squared	0.999550
10.6	276	No. of Observations	5
		Degrees of Freedom	3

X Coefficient(s) 0.038293  
Std Err of Coef. 0.000468

## Ethyl Acetate

Conc	Peak Hgt		Regression Output:
0.197	7		
0.983	28	Constant	-0.12914
1.97	51	Std Err of Y Est	0.057703
4.92	126	R Squared	0.999837
9.83	244	No. of Observations	5
		Degrees of Freedom	3

X Coefficient(s) 0.040670  
Std Err of Coef. 0.000298

## Propanol

Conc	Peak Hgt		Regression Output:
0.192	10		
0.481	22	Constant	-0.00864
0.962	44	Std Err of Y Est	0.017081
1.93	90	R Squared	0.999937
4.81	222	No. of Observations	5
		Degrees of Freedom	3

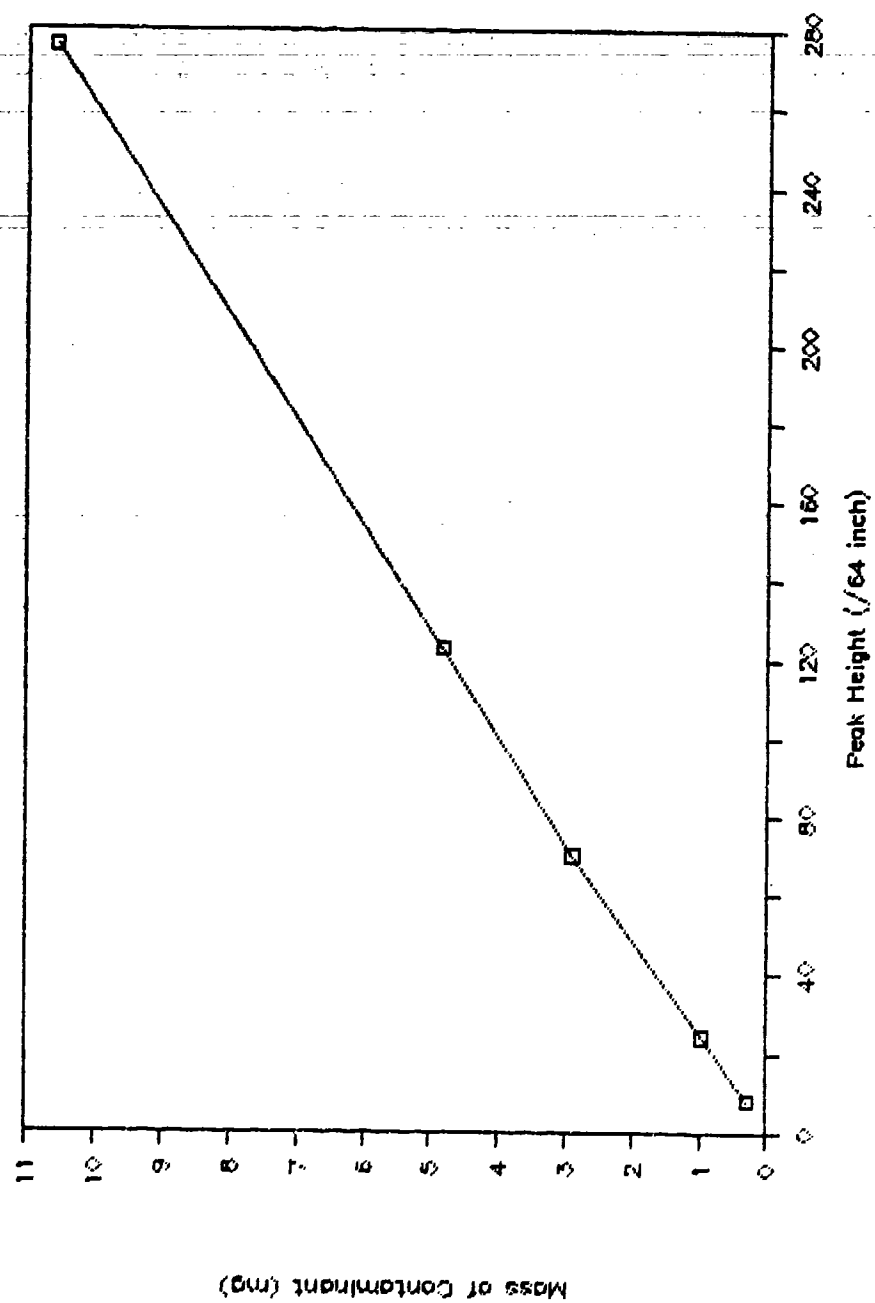
X Coefficient(s) 0.021696  
Std Err of Coef. 0.000098

## 2-Methoxyethanol

Conc	Peak Hgt		Regression Output:
0.193	4		
0.386	11.5	Constant	-0.04071
1.93	56	Std Err of Y Est	0.149031
3.86	116	R Squared	0.998283
7.73	216	No. of Observations	5
		Degrees of Freedom	3

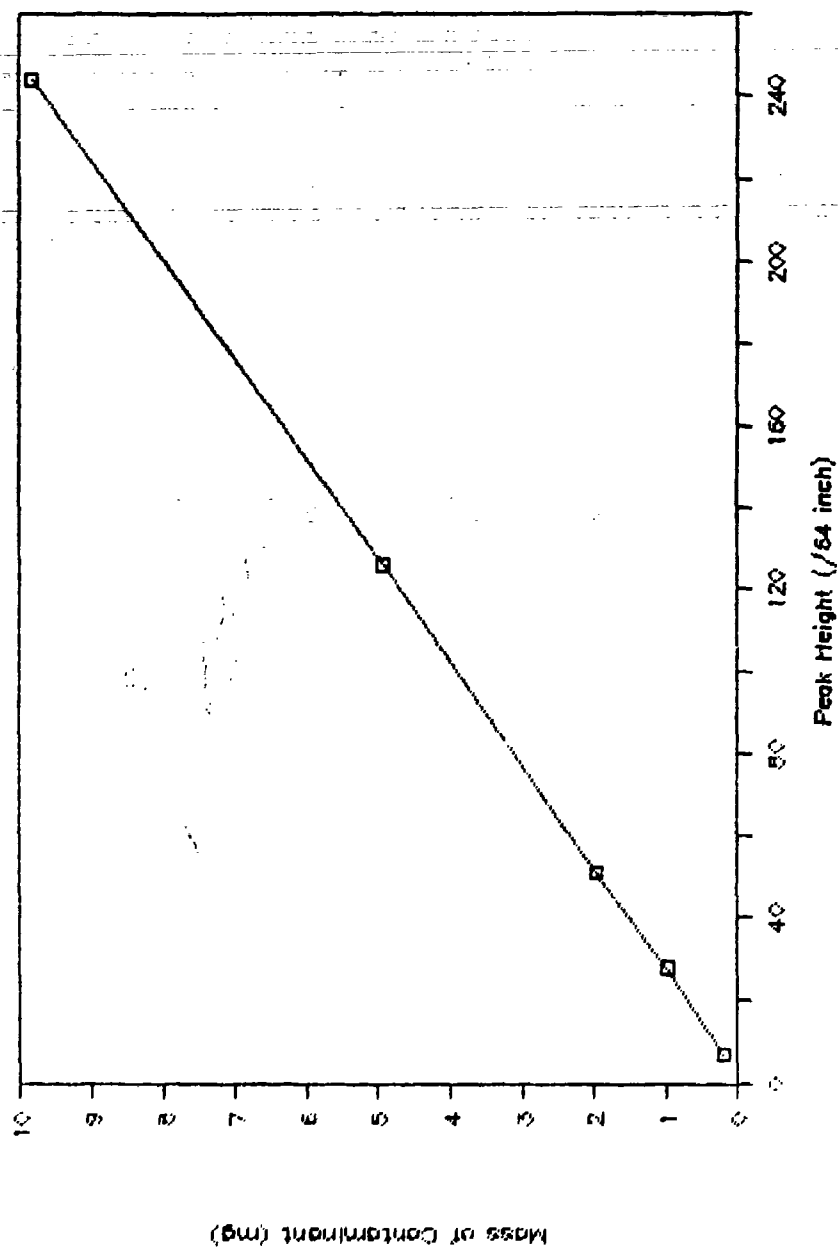
X Coefficient(s) 0.035446  
Std Err of Coef. 0.000848

## Ethyl Ether Calibration Curve

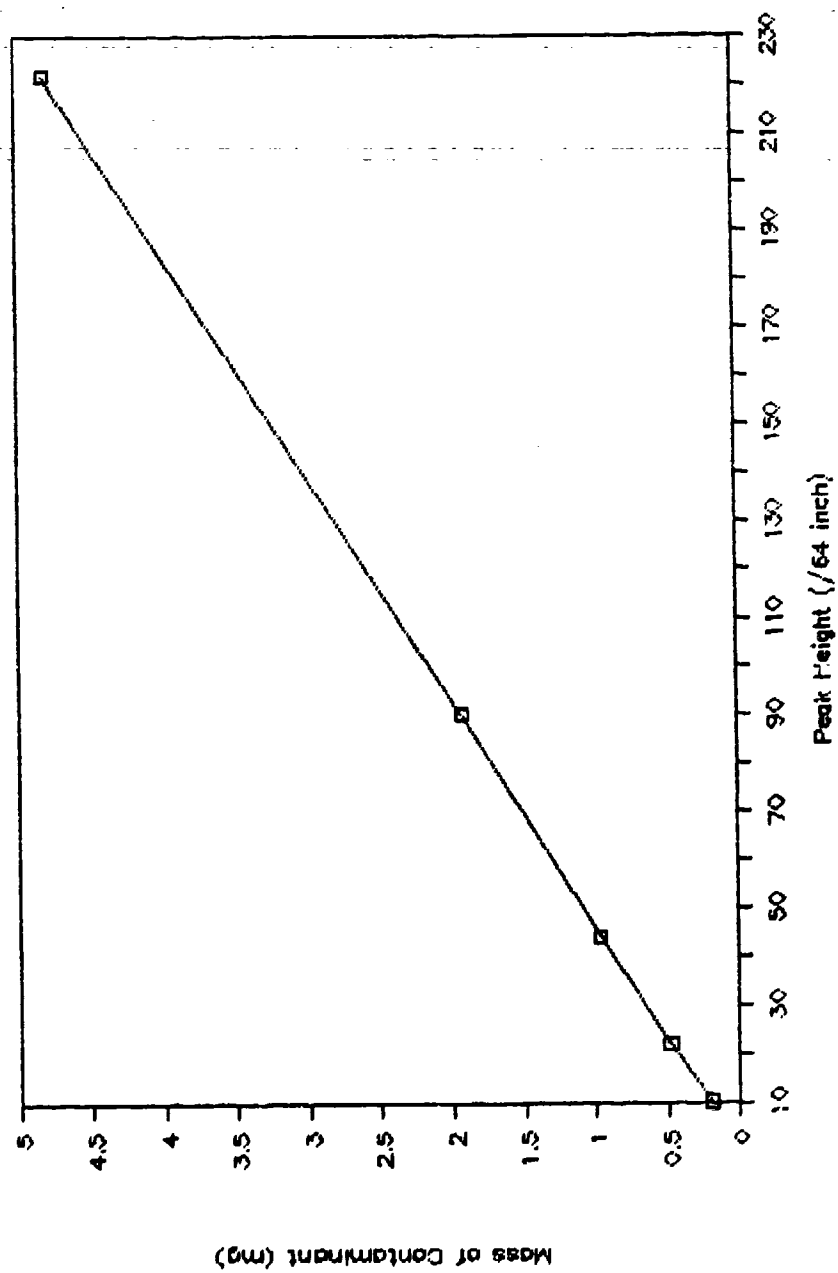




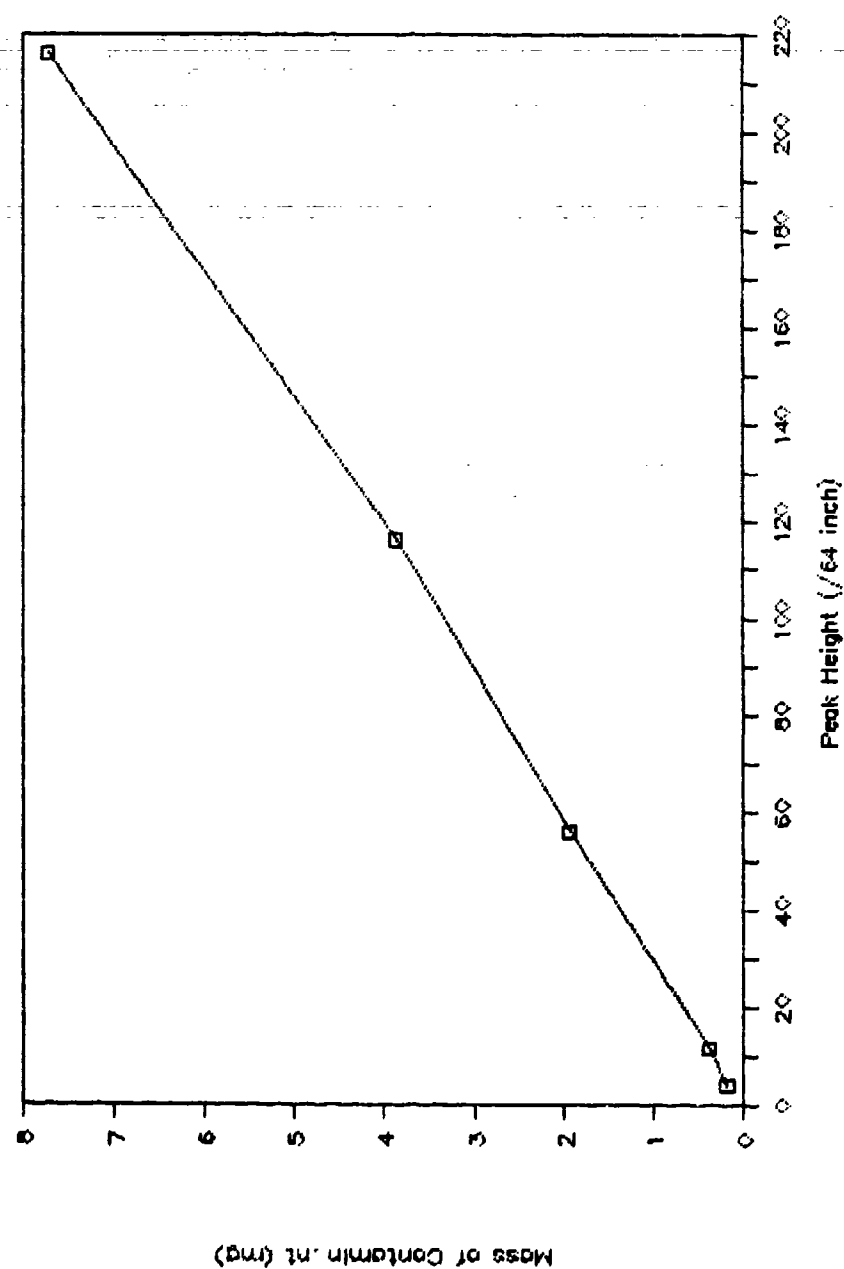
Ethyl Acetate Calibration Curve



2-Propanol Calibration Curve



2-Methoxyethanol Calibration Curve



**APPENDIX F**

TABLE F1

## Desorption Efficiencies for Charcoal Tubes

## Ethyl Ether

Mass Injected (mg) Mass Recovered (mg) Desorption Efficiency

0.707	0.726	102.7
0.707	0.649	91.9
0.707	0.688	97.3

3.533	2.794	79.1
3.533	2.870	81.2
3.533	2.947	83.4

7.066	5.704	80.7
7.066	5.819	82.4
7.066	5.742	81.3

10.599	8.538	80.6
10.599	8.423	79.5
10.599	8.614	81.3

14.132	11.180	79.1
14.132	11.142	78.8
14.132	11.295	79.9

Overall Mean: 84.0

TABLE F2

## Desorption Efficiencies for Charcoal Tubes

## Ethyl Acetate

Mass Injected (mg) Mass Recovered (mg) Desorption Efficiency

0.894	0.847	94.7
0.894	0.847	94.7
0.894	0.806	90.2
2.682	2.596	96.8
2.682	2.555	95.3
2.682	2.474	92.2
4.47	4.223	94.5
4.47	4.304	96.3
4.47	4.223	94.5
6.258	6.012	96.1
6.258	5.931	94.8
6.258	6.053	96.7
8.94	8.737	97.7
8.94	8.696	97.3
8.94	8.656	96.8

Overall Mean: 95.2

TABLE F3

## Desorption Efficiencies for Charcoal Tubes

## Propanol

Mass Injected (mg) Mass Recovered (mg) Desorption Efficiency

0.802	0.794	99.0
0.802	0.794	99.0
0.802	0.772	96.3
1.604	1.553	96.9
1.604	1.575	98.2
1.604	1.532	95.5
3.208	3.094	96.4
3.208	3.050	95.1
3.208	3.029	94.4
4.812	4.548	94.5
4.812	4.591	95.4
4.812	4.526	94.1
6.416	6.023	93.9
6.416	6.066	94.6
6.416	5.936	92.5

Overall Mean: 95.7

TABLE F4

## Desorption Efficiencies for Charcoal Tubes

## 2-Methoxyethanol

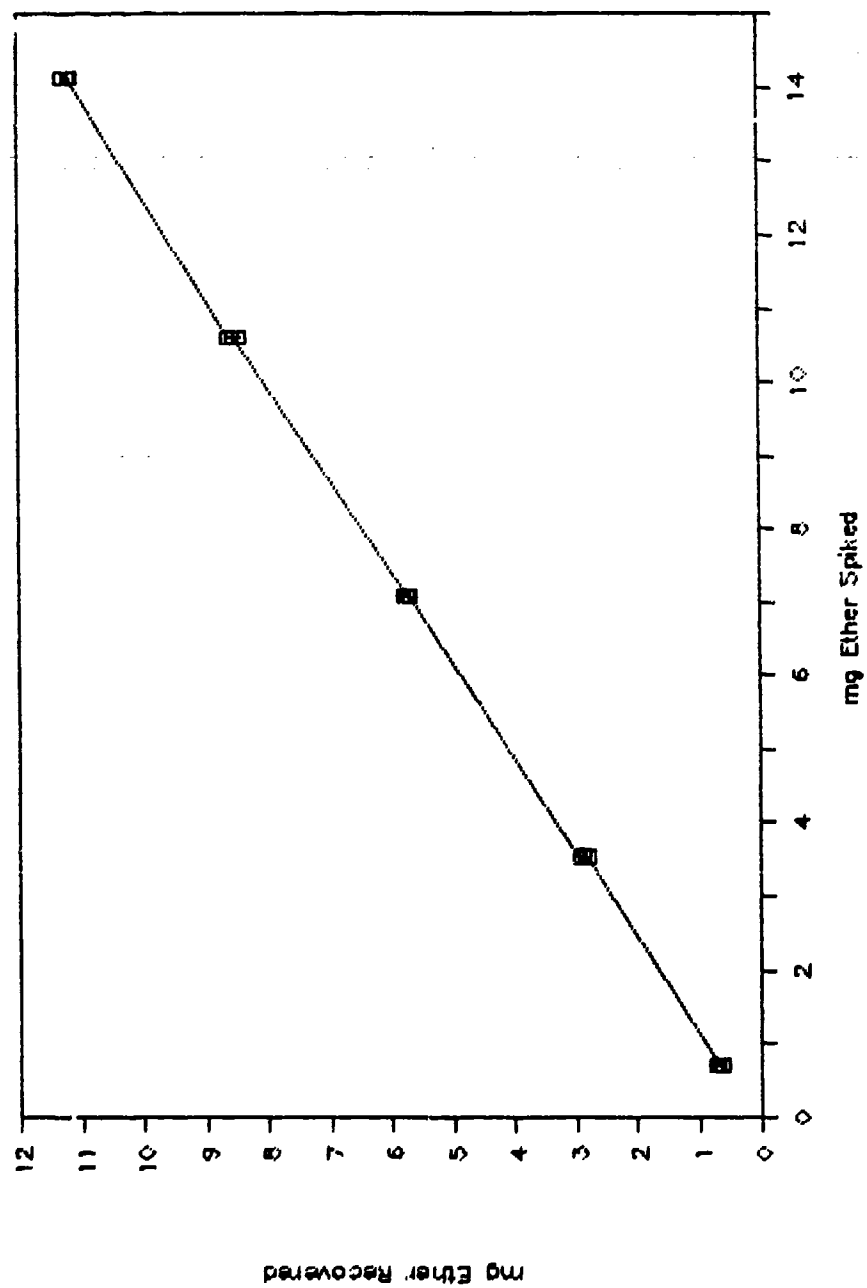
Mass Injected (mg) Mass Recovered (mg) Desorption Efficiency

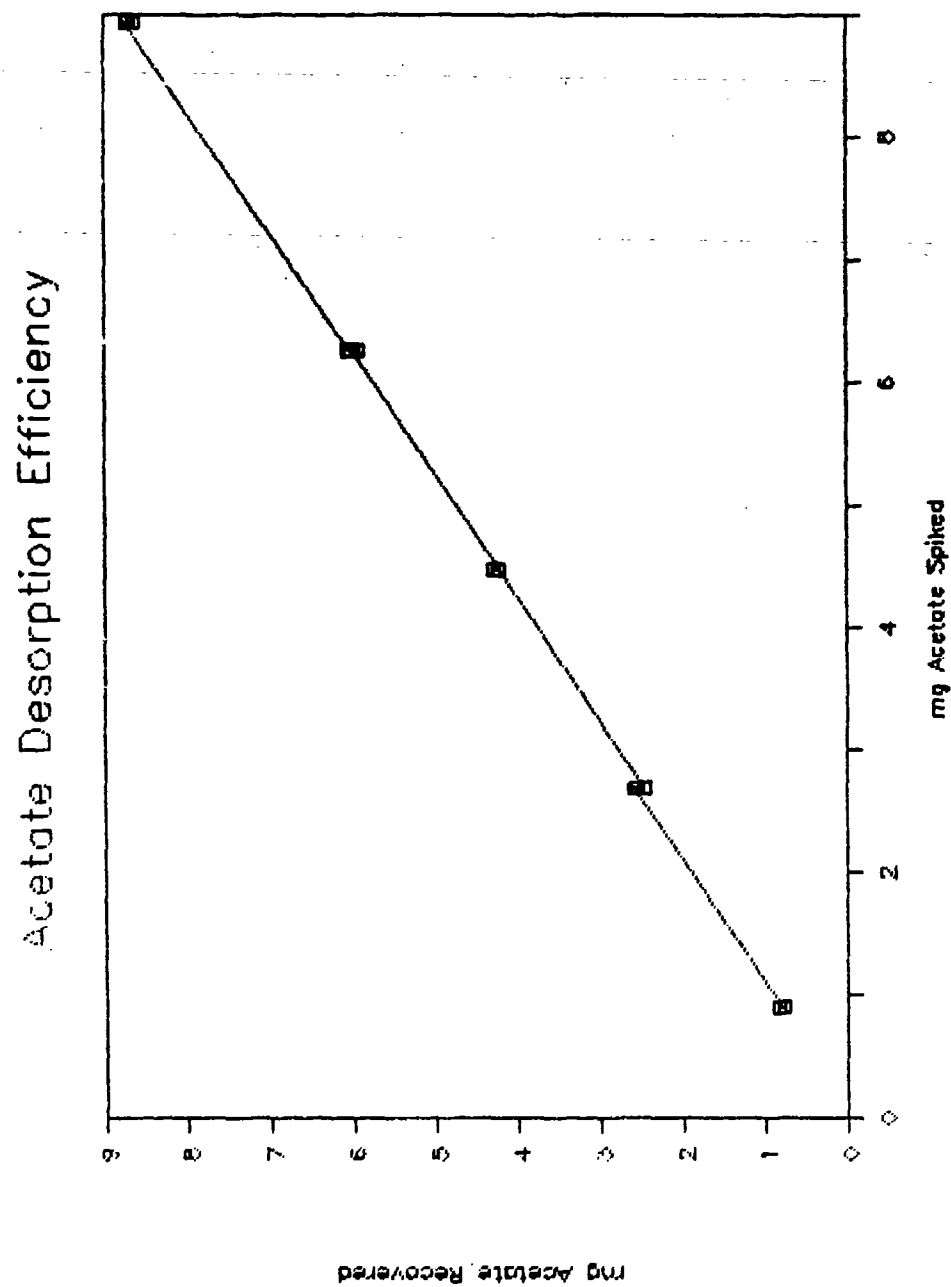
0.966	0.881	91.2
0.966	0.899	93.0
0.966	0.916	94.9
1.932	1.873	97.0
1.932	1.838	95.1
1.932	1.838	97.0
2.898	2.830	97.7
2.898	2.760	95.2
2.898	2.724	94.0
4.83	4.638	96.0
4.83	4.603	95.3
4.83	4.709	97.5
5.796	5.631	97.2
5.796	5.595	96.5
5.796	5.631	97.2

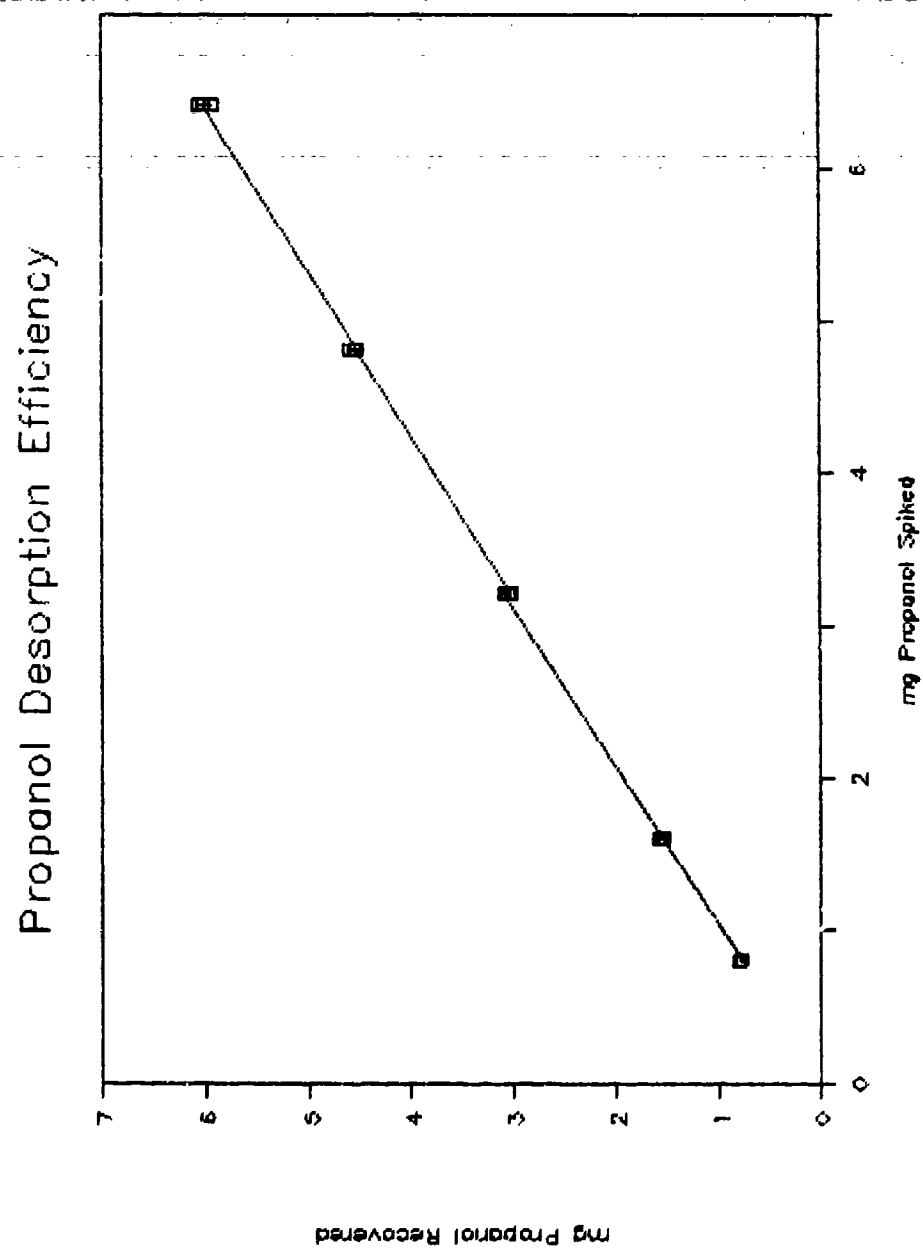
Overall Mean: 95.5



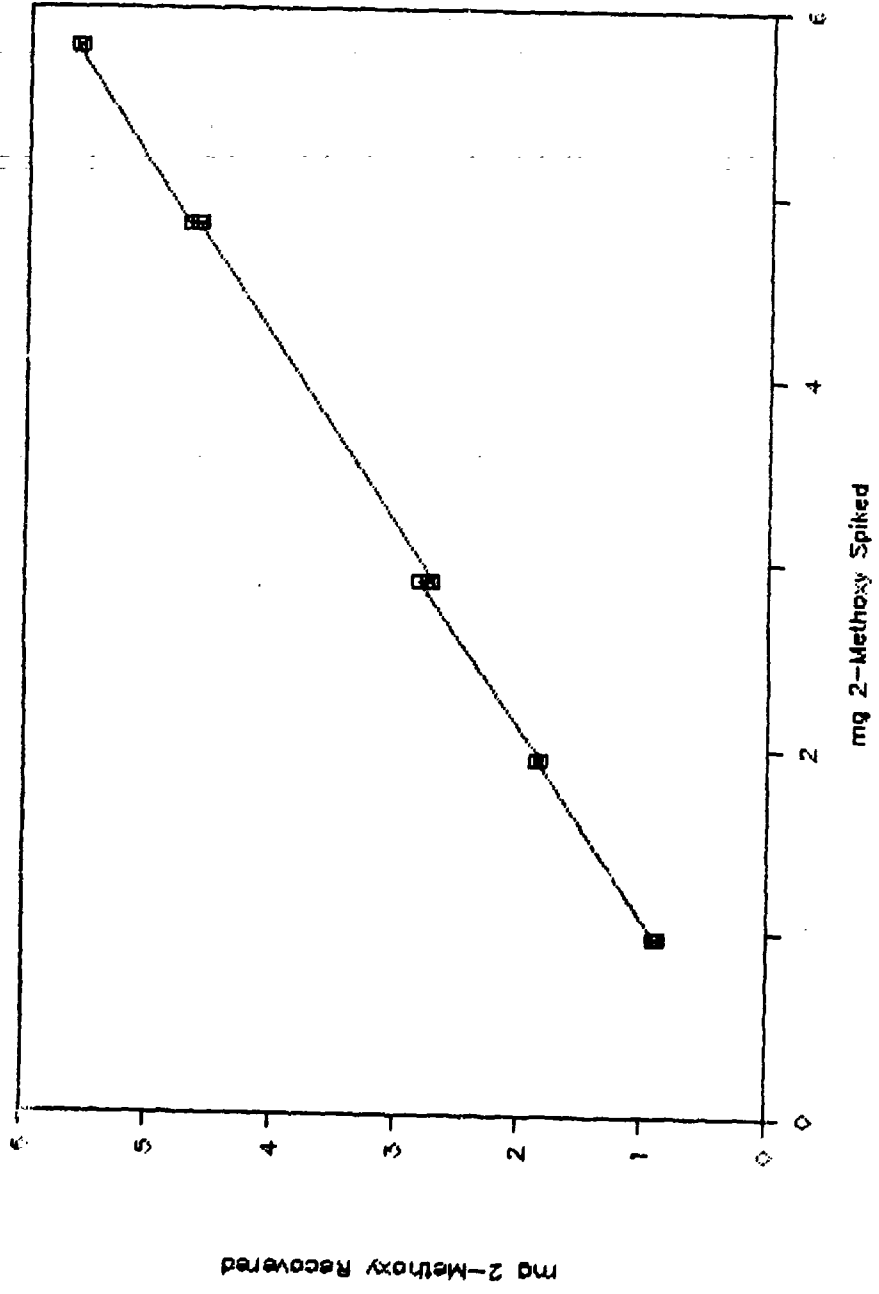
## Ether Desorption Efficiency







# 2-Methoxy Desorption Efficiency



**APPENDIX G**

### Sample Concentration Calculation

Solvent:	Ethyl Actetate
Average GC Peak Height:	28 mm
Sample Recovery:	1.00962 mg
Desorption Efficiency:	0.9524
Corrected Sample Recovery:	1.060079 mg
Sample Volume:	4.396 liters
Calculated Conc (mg/M <sup>3</sup> ):	$\frac{(1.06)(10^3)}{4.396} = 241.15$
Concentration (ppm):	$\frac{(241.15)(273)(761.18)}{(88.11)(22.4)(760)(292.6)} = 65.61$
Actual Concentration (ppm):	101.91
Collection Efficiency:	$65.61/101.91 = 0.6438$

**APPENDIX H**

NOTE: COPYRIGHT (C) 1984, 1988 SAS INSTITUTE INC., CARY, N.C. 27512, U.S.A.  
 NOTE: THE JOB BOB HAS BEEN RUN UNDER RELEASE 9.18 OF SAS AT TEXAS A&M UNIVERSITY (01455001).

NOTE: CPUID VERSION = 21 SERIAL = 172328 MODEL = 3090  
 CPUID VERSION = 21 SERIAL = 272328 MODEL = 3090

NOTE: SAS OPTIONS SPECIFIED ARE:  
 SORT=4

```
1 DATA ONE;
2 INPUT COLLEFF HUMID CONC COMPTYPE POL SOL INSTR;
3 IF 79 LE HUMID LE 82 THEN HUMIDGRP=80;
4 ELSE HUMIDGRP=50;
5 CARDS;
```

NOTE: DATA SET WORK.ONE HAS 48 OBSERVATIONS AND 8 VARIABLES. 690 OBS/TRK.  
 NOTE: THE DATA STATEMENT USED 0.03 SECONDS AND 132K.

```
54 *****
55 PROC PRINT DATA=ONE;
56 NOTE: THE PROCEDURE PRINT USED 0.06 SECONDS AND 196K AND PRINTED PAGE 1.
```

```
56 PROC UNIVARIATE FREQ DATA=ONE;
```

```
57 NOTE: THE PROCEDURE UNIVARIATE USED 0.08 SECONDS AND 180K AND PRINTED PAGES 2 TO 8
```

```
57 PROC GLM DATA=ONE;
58 CLASSES HUMIDGRP CONC INSTR COMPTYPE;
59 MODEL COLLEFF = HUMIDGRP;
60 MEANS HUMIDGRP;
```

```
61 NOTE: THE PROCEDURE GLM USED 0.09 SECONDS AND 420K AND PRINTED PAGES 9 TO 11.
```

```
61 PROC GLM DATA=ONE;
62 CLASSES HUMIDGRP CONC INSTR COMPTYPE;
63 MODEL COLLEFF = CONC;
64 MEANS CONC;
```

```
65 NOTE: THE PROCEDURE GLM USED 0.09 SECONDS AND 420K AND PRINTED PAGES 12 TO 14.
```

```
65 PROC GLM DATA=ONE;
66 CLASSES HUMIDGRP CONC INSTR COMPTYPE;
67 MODEL COLLEFF=INSTR;
68 MEANS INSTR/LSD;
```

```
69 NOTE: THE PROCEDURE GLM USED 0.10 SECONDS AND 420K AND PRINTED PAGES 15 TO 17.
```

```
69 PROC GLM DATA=ONE;
70 CLASSES HUMIDGRP CONC INSTR COMPTYPE;
71 MODEL COLLEFF=COMPTYPE;
72 MEANS COMPTYPE/LSD;
```

```
73 NOTE: THE PROCEDURE GLM USED 0.10 SECONDS AND 420K AND PRINTED PAGES 18 TO 20.
```

```
73 PROC GLM DATA=ONE;
74 CLASSES HUMIDGRP CONC INSTR COMPTYPE;
75 MODEL COLLEFF = HUMIDGRP CONC HUMIDGRP*CONC;
76 MEANS HUMIDGRP CONC/LSD;
```



77 NOTE: THE PROCEDURE GLM USED 0.10 SECONDS AND 420K AND PRINTED PAGES 21 TO 24.

77 PROC GLM DATA=ONE;  
78 CLASSES HUMIDGRP CONC INSTR COMPTYPE;  
79 MODEL COLLEFF = HUMIDGRP COMPTYPE;  
80 MEANS HUMIDGRP COMPTYPE/LSD;  
81

NOTE: THE PROCEDURE GLM USED 0.10 SECONDS AND 420K AND PRINTED PAGES 25 TO 28.

81 PROC GLM DATA=ONE;  
82 CLASSES HUMIDGRP CONC INSTR COMPTYPE;  
83 MODEL COLLEFF = CONC COMPTYPE;  
84 MEANS CONC COMPTYPE/LSD;  
85

NOTE: THE PROCEDURE GLM USED 0.10 SECONDS AND 420K AND PRINTED PAGES 29 TO 32.

85 PROC GLM DATA=ONE;  
86 CLASSES HUMIDGRP CONC INSTR COMPTYPE;  
87 MODEL COLLEFF = HUMIDGRP CONC HUMIDGRP\*CONC COMPTYPEE  
88 HUMIDGRP\*COMPTYPE CONC\*COMPTYPE  
89 HUMIDGRP\*CONC\*COMPTYPE;  
90 MEANS HUMIDGRP CONC COMPTYPE/LSD;

NOTE: THE PROCEDURE GLM USED 0.17 SECONDS AND 420K AND PRINTED PAGES 33 TO 37.

91 PROC REG DATA=ONE;  
92 MODEL COLLEFF = HUMID CONC POL;  
93

NOTE: THE PROCEDURE REG USED 0.06 SECONDS AND 432K AND PRINTED PAGE 38.  
NOTE: SAS USED 432K MEMORY.

NOTE: SAS INSTITUTE INC.  
SAS CIRCLE  
PO BOX 8000  
CARY, N.C. 27512-8000

## SAS

## GENERAL LINEAR MODELS PROCEDURE

## CLASS LEVEL INFORMATION

CLASS	LEVELS	VALUES
HUMIDGRF	2	50 80
CONC	2	50 200
INSTR	5	1 2 3 4 6
COMPTYPE	4	ACETATE ETHER PROPANOL 2METHOXY

NUMBER OF OBSERVATIONS IN DATA SET = 48

## SAS

## GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: COLLEFF								
SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.	
MODEL	4	0.16481786	0.04123696	0.45	0.7746	0.039839	45.1383	
ERROR	43	3.97537468	0.09245057		ROOT MSE		COLLEFF MEAN	
CORRECTED TOTAL	47	4.14032254			0.30405686		0.67361204	
SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
INSTR	4	0.16484786	0.45	0.7746	4	0.16484786	0.45	0.7746

## SAS

## GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: COLLEFF

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	15	4.10166544	0.27344436	226.35	0.0001	0.990663	5.1598
ERROR	32	0.0365711	0.00120803		ROOT MSE		COLLEFF MEAN
CORRECTED TOTAL	47	4.14032254			0.03475679		0.67361204

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
HUMIDGRP	1	0.04815487	39.86	0.0001	1	0.04815487	39.86	0.0001
CONC	1	0.08186536	67.77	0.0001	1	0.08186536	67.77	0.0001
HUMIDGRP*CONC	1	0.00823718	6.82	0.0136	1	0.00823718	6.82	0.0136
COMPTYPE	3	3.40751946	940.24	0.0001	3	3.40751946	940.24	0.0001
HUMIDGRP*COMPTYPE	3	0.13187586	36.39	0.0001	3	0.13187586	36.39	0.0001
CONC*COMPTYPE	3	0.39554069	109.14	0.0001	3	0.39554069	109.14	0.0001
HUMIDGRP*CONC*COMPTYPE	3	0.02847183	7.86	0.0005	3	0.02847183	7.86	0.0005

SAS

## GENERAL LINEAR MODELS PROCEDURE

T TESTS (LSD) FOR VARIABLE: COLLEFF  
 NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE.  
 NOT THE EXPERIMENTWISE ERROR RATE

ALPHA=0.05 DF=32 MSE=0.001208  
 CRITICAL VALUE OF T=2.03693  
 LEAST SIGNIFICANT DIFFERENCE=.02044

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T	GROUPING	MEAN	N	HUMIDGRP
	A	0.70529	24	50
	B	0.64194	24	6J

## SAS

## GENERAL LINEAR MODELS PROCEDURE

T TESTS (LSD) FOR VARIABLE: COLLEFF  
 NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE.  
 NOT THE EXPERIMENTWISE ERROR RATE

ALPHA=0.05 DF=32 MSE=0.001208  
 CRITICAL VALUE OF T=2.03693  
 LEAST SIGNIFICANT DIFFERENCE=.02044

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T	GROUPING	MEAN	N	CONC
	A	0.71491	24	200
	B	0.63231	24	50

## SAS

## GENERAL LINEAR MODELS PROCEDURE

T TESTS (LSD) FOR VARIABLE: COLLEFF  
 NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE.  
 NOT THE EXPERIMENTWISE ERROR RATE

ALPHA=0.05 DF=32 MSE=0.001208  
 CRITICAL VALUE OF T=2.03693  
 LEAST SIGNIFICANT DIFFERENCE=0.0289

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T	GROUPING	MEAN	N	COMPTYPE
	A	1.13383	12	ETHER
	B	0.54294	12	ACETATE
	B	0.52857	12	2METHOXY
	C	0.48911	12	PROPANOL

SAS  
GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: COLLEFF

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	3	0.11286518	0.03762173	77.54	0.0001	0.966752	4.1673
ERROR	8	0.00388165	0.00048521		ROOT MSE		COLLEFF MEAN
CORRECTED TOTAL	11	0.11674683			0.02202741		0.52857117

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
HUMIDGRP	1	0.00136410	2.81	0.1321	1	0.00136410	2.81	0.1321
CONC	1	0.09575711	197.35	0.0001	1	0.09575711	197.35	0.0001
HUMIDGRP*CONC	1	0.01574396	32.45	0.0005	1	0.01574396	32.45	0.0005



SAS  
GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: COLLEFF

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	3	0.12223433	0.04074478	91.82	0.0001	0.971776	4.3070
ERROR	8	0.00355010	0.00044376		ROOT MSE		COLLEFF MEAN
CORRECTED TOTAL	11	0.12578443			0.02105567		0.48910683

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
HUMIDGRP	1	0.10735965	241.83	0.0001	1	0.10735965	241.83	0.0001
CONC	1	0.01458650	33.12	0.0004	1	0.01458650	33.12	0.0004
HUMIDGRP*CONC	1	0.00017818	0.40	0.5440	1	0.00017818	0.40	0.5440

SAS  
GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: COLLEFF

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.
MODEL	3	0.25684363	0.08561454	109.54	0.0001	0.976234	5.1502
ERROR	8	0.00528511	0.00066064		ROOT MSE		COLLEFF MEAN
CORRECTED TOTAL	11	0.26319874			0.02796227		0.54283575

SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
HUMIDGRP	1	0.00982055	12.69	0.0074	1	0.00982055	12.69	0.0074
CONC	1	0.24328157	311.15	0.0001	1	0.24328157	311.15	0.0001
HUMIDGRP*CONC	1	0.00374141	4.79	0.0602	1	0.00374141	4.79	0.0602

## SAS

## GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: COLLEFF						
SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE
MODEL	3	0.18473814	0.06157938	17.34	0.0013	0.881413
ERROR	7	0.02485491	0.00355070		ROOT MSE	COLLEFF MEAN
CORRECTED TOTAL	10	0.20859305			0.05958776	1.14534200
		TYPE I SS	F VALUE	PR > F	DF	F VALUE
SOURCE	DF	TYPE I SS	F VALUE	PR > F	DF	PR > F
HUMIDGRP	1	0.04794429	13.38	0.0041	1	0.0053
CONC	1	0.12281081	34.62	0.0006	1	0.0008
HUMIDGRP*CONC	1	0.01428304	4.02	0.0448	1	0.0448

SAS  
GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE: COLLEFF									
SOURCE		DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PR > F	R-SQUARE	C.V.	
MODEL		11	0.51068845	0.04642622	81.41	0.0001	0.973899	4.5906	
ERROR		24	0.0158686	0.00057029		ROOT MSE		COLLEFF MEAN	
CORRECTED TOTAL		35	0.52437531			0.02388066		0.52020458	
SOURCE		DF	TYPE I SS	F VALUE	PR > F	DF	TYPE III SS	F VALUE	PR > F
HUMIDGRP		1	0.01217584	21.35	0.0001	1	0.01217584	21.35	0.0001
CONC		1	0.28453743	498.94	0.0001	1	0.28453743	498.94	0.0001
HUMIDGRP*CONC		1	0.00086562	1.52	0.2289	1	0.00086562	1.52	0.2289
COMPTYPE		2	0.01864531	16.35	0.0001	2	0.01864531	16.35	0.0001
HUMIDGRP*COMPTYPE		2	0.10646856	93.35	0.0001	2	0.10646856	93.35	0.0001
CONC*COMPTYPE		2	0.06918776	60.67	0.0001	2	0.06918776	60.67	0.0001
HUMIDGRP*CONC*COMPTYPE		2	0.01879793	16.48	0.0001	2	0.01879793	16.48	0.0001

## SAS

## GENERAL LINEAR MODELS PROCEDURE

T TESTS (LSD) FOR VARIABLE: COLLEFF  
 NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE.  
 NOT THE EXPERIMENTWISE ERROR RATE

ALPHA=0.05 DF=24 MSE=5.7E-04  
 CRITICAL VALUE OF T=2.06390  
 LEAST SIGNIFICANT DIFFERENCE=.01643

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T	GROUPING	MEAN	N	CONC
	A	0.009108	18	200
	B	0.431301	18	50

## SAS

## GENERAL LINEAR MODELS PROCEDURE

T TESTS (LSO) FOR VARIABLE: COLLEFF  
 NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE.  
 NOT THE EXPERIMENTWISE ERROR RATE

ALPHA=0.05 DF=24 MSE=5.7E-04  
 CRITICAL VALUE OF T=2.06390  
 LEAST SIGNIFICANT DIFFERENCE=.01643

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T	GROUPING	MEAN	N	HUMIDGRP
	A	0.538595	18	50
	B	0.501814	18	30

## SAS

## GENERAL LINEAR MODELS PROCEDURE

T TESTS (LSD) FOR VARIABLE: COLLEFF  
 NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,  
 NOT THE EXPERIMENTWISE ERROR RATE

ALPHA=0.05 DF=24 MSE=5.7E-04  
 CRITICAL VALUE OF T=2.06390  
 LEAST SIGNIFICANT DIFFERENCE=.02012

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T	GROUPING	MEAN	N	COMTYPE
	A	0.542936	12	ACETATE
	A			
	A	0.528571	12	2METHOXY
	B	0.489107	12	PROPANOL

**VITA**

Robert Bruce Walton, son of George and Marty Walton, was born in Philadelphia, Pennsylvania on December 27, 1960. He graduated from Oscoda Area High School in May of 1978. He attended Texas A&M University in College Station, Texas and received a Bachelor of Science degree in Bioengineering in August of 1984. He joined the United States Air Force in October of 1984 and was stationed at Cannon Air Force Base in Clovis, New Mexico. He began to pursue a Master of Science degree in Industrial Hygiene at Texas A&M University in August of 1988. He is currently employed as an industrial hygiene consultant with the United States Air Force at The Occupational and Environmental Health Laboratory (OEHL) on Brooks Air Force Base.